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MODULATION INDUCING RETRODIRECTIVE OPTICAL SYSTEM (MIROS) FOLLOWON PROGRAM

Prepared under Contract No. NAS 5-9764 by
WESTINGHOUSE DEFENSE AND SPACE CENTER
Baltimore, Md.
for Goddard Space Flight Center

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION • WASHINGTON, D. C. • MARCH 1966



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FOREWORD

This report was prepared by the Westinghouse Defense and Space Center, Aerospace Division, Baltimore, Maryland, under National Aeronautics and Space Administration contract number NAS 5-9764. It covers a 3-month experimental and research program to determine phenomena and techniques applicable to completely passive intelligence transfer by optical means.

Administration of the program by the monitoring agency was under the cognizance of Dr. Henry Plotkin, Goddard Space Flight Center. The program was conducted at the Westinghouse Aerospace Division under the technical direction of Mr. J. B. Goodell, Fellow Engineer, Optical Maser Systems; Mr. C. R. Kline, Manager.

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ABSTRACT

This report is the result of a 3-month followon to the MIROS program (NASw 703). These two programs were initiated in order to study passive modulation of light by light. This report describes the results of a research of materials which are potentially able to generate absorption bands upon optical irradiation and the result of an experimental study of the possibility of using an alkali halide as a passive modulation transfer element.

A search of the literature has revealed many organic compounds which generate absorption bands upon irradiation. Induced absorption by means of generating free-charge carriers in a photoconductive material is discussed. Uranyl compounds also have been looked into as possible devices. The experimental results of passive modulation using alkali halides indicates that they are not ideal modulation transfer devices.

It is concluded that a passive optical modulation transfer can be accomplished at frequencies not exceeding a few megacycles. Power requirements on the optical beams are moderate, on the order of milliwatts.

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1. INTRODUCTION

This report is the result of a 3-month followon to the original MIROS program. The objective of the original MIROS program (contract number NASw 703) was to study, experimentally and theoretically, the possibility of passive modulation transfer between two optical beams. During the first MIROS program, passive optical modulation was experimentally demonstrated in a mercury absorption cell containing a small amount of nitrogen. In this experiment, it was shown that the mercury resonance line (2537 Å) not only could cause a marked absorption of the mercury 4047 Å line, but that the frequency response of this system was satisfactory for communication purposes. A disadvantage of this system was that it could only operate at these two wavelengths.

A study of the possibility of using the alkali halides was also made. During the first MIROS program, however, there was not sufficient time to determine experimentally the feasibility of passive modulation transfer with alkali-halide crystals. Therefore, a 3-month followon program was initiated with a twofold purpose: (1) to study other materials which might offer the possibility of passive modulation transfer at many arbitrary wavelengths, and (2) to demonstrate conclusively by experiments whether or not passive optical modulation transfer is feasible using alkali-halide crystals.

As a result of this effort, many organic compounds have been listed in which absorption bands can be induced by flash photolytic methods. These compounds are usually ignored in physical applications of luminescence because of their low dissociation energies, but in a MIROS system, where incident energies are necessarily quite small, they could be ideal. Some other passive modulation transfer schemes are also considered in this report. One is modulation by the injection of free-charge carriers in a semiconductor.

Finally, it has been concluded that alkali-halide crystals do not make practical modulation transfer elements. Although a new absorption band was produced upon irradiation of the crystal, the effect left much to be desired for an effective communications system.

In the entire MIROS program, emphasis was upon passively modulating light by light, using one beam to create new absorption bands, thus increasing the optical density for a second beam. This was accomplished when the first beam of light initiated a series of energy-level transitions, leading to an increase in the population of a metastable energy level or a conduction band population.

The MIROS technical data report ⁷⁰ contains detailed mathematical discussions of the parameters involved in a system using these principles. This report is not meant to be a second theoretical treatment, so mathematics are used only where necessary to illustrate certain points, and in these cases, only basic equations are stated. In this report, the emphasis has been on materials research and experimental results.

2. GENERAL REMARKS

In this report, it is assumed that optical absorption follows the simple Lambert's law; i.e., $I = I_0 e^{-k\ell}$, where I_0 is the initial intensity and I is the intensity after traversing a layer of substance of length ℓ , whose absorption coefficient is k . Perhaps a more instructive form of the equation for the present report is the differential form; i.e., $dI = -kI d\ell$, since k itself may be a function of coordinates. In this case, the integrated form of the law is:

$$I = I_0 e^{-\int_0^{\ell} k(x) dx}$$

which reduces to the simple form for constant k . Actually, Lambert's law can be thought of as expressing a probability; i.e., the probability that a photon is absorbed is proportional to the number of photons present.

In considering the MIROS system, it is necessary to keep in mind the fact that absorption follows this exponential law and is not a linear function. While this point may seem trite, it is important since it will be the absorption coefficient and not absorption itself that will be linearly altered. A simple example will illustrate the idea. Differentiate the intensity with respect to the absorption coefficient.

$$\Delta I = -I_0 x e^{-kx} \Delta k$$

Evidently, a 10-percent change, say in k , will not, in general, result in a 10-percent change in I . If a high amount of absorption is initially present, an enormous change in k might be required to produce a perceptible change in I .

Since in the present scheme modulation of the "read" beam takes the form of induced absorption, it is necessary to determine how much absorption will result from populating an energy level. It is well known that the absorption coefficient is nearly proportional to the density of atoms in the lower state.

If large powers of light irradiate the absorption cell, this proportionality no longer holds since the upper state population affects the absorption process. This effect becomes strikingly evident in lasers. For the MIROS system, however, where it is expected that only small radiative powers will strike the element, the ground state population will always far exceed that of the other levels, so the approximation may be taken with impunity in most cases. The absorption coefficient will therefore be broken into two parts; the cross section per atom and the density of atoms (i. e., $k = \sigma N$). Now it becomes explicitly clear why care must be used in defining absorption changes, since one photon absorbed from the "write" beam resulting (in the most efficient case) in one electron populating the metastable energy level will not, in general, result in one photon being removed from the "read" beam. The change in absorption in going from 0 to 1 electron per cubic centimeter is

$$I_0 \left[1 - e^{-\sigma \ell} \right] .$$

In a typical example, let $\sigma = 10^{-13} \text{ cm}^2/\text{atom/cc}$ and $\ell = 1 \text{ cm}$. Then to induce 50-percent absorption,

$$e^{-10^{-13} N} = 0.5,$$

or

$$10^{-13} N = 0.693$$

and

$$N = 6.93 \times 10^{12} \text{ atoms/cc}.$$

Actually, the simple equation $dI = -I\sigma N dx$ represents the statement of the principle of optical modulation by means of induced absorption. What remains is to determine expressions for σ and N . This is not always easy, but in some cases reasonable approximations can be made. The cross section can be determined from transition probabilities and does not present too great a problem. See, for example, Mitchell and Zemansky, Resonance Radiation and Excited Atoms⁶⁶ for a discussion of absorption coefficients and their

calculations. There is no fixed recipe for determining the population density of a given energy level, as there are many situations, each requiring a different approach. Usually rate equations are setup, the number of equations corresponding to the number of energy levels involved in the process. Since in some cases many levels are involved, the number of equations may become impractically large. In such cases, approximations may be sought. Evidently, the number of atoms per centimeter that can be made to populate an energy level will depend inversely on the average lifetime of that level. This is why metastable energy levels seem attractive. Because of their long lifetimes, metastable energy levels should act as ground states for higher optical transitions. A classical example of induced absorption in a gas is the induced absorption of the mercury 4049 Å line when the mercury resonance line irradiates a mercury absorption cell containing a few millimeters of nitrogen at room temperature. This system was discussed in detail in MIROS technical data report (contract number NASw 703). The ground state of mercury is a singlet (1S_0), while the first excited is a triplet (3P_0). Transitions between these two states are normally forbidden according to the usual rules of Russell-Sanders coupling, but because of the high atomic number of mercury, there is sufficient mixing of the wave functions between these two states that the transition corresponding to the strong 2537 Å line is allowed. However, the state lying about 0.2 electron volt below the 3P_1 state does not mix with the singlet ground, and as a result, $^3P_0 \longrightarrow ^1S_0$ transitions are highly forbidden. The 3P_0 state is therefore metastable with lifetime of the order of 10^{-2} to 10^{-3} seconds.

This ideal situation makes possible one passive optical modulation scheme; namely, atoms are raised from ground to first excited by absorption of 2537 Å radiation, from which they fall to the 3P_0 metastable by losing the 0.2 electron volt in collisions with nitrogen molecules. Once in the metastable level, they absorb the mercury 4047 Å line and are raised to the 3S_1 state. That such a mechanism is possible was demonstrated early in the history of spectroscopy

by Gaviola, Wood, Pringsheim, Samson, and others when they showed that addition of pure nitrogen to a mercury lamp cell resulted in strong self-reversal of the 4047 Å line.

To formulate this particular problem requires considering at least 5 energy levels: 6^1S_0 , 6^3P_2 , 6^3P_1 , 6^3P_0 , and 7^3S_1 . This represents considerable awkwardness in the mathematical expressions, so approximations are sought, in order to obtain expressions which are simple enough to interpret but accurate enough to be useful. It is found that, for sufficient accuracy, only the 3P_1 and 3P_0 state populations need be considered, as the ground state is always much more strongly populated than any of the others, and therefore can be considered constant, while other populations contribute negligibly to the process.

3. METASTABLE ENERGY LEVELS

The question of the desirability of seeking metastable energy levels naturally arises in a consideration of the MIROS scheme. The possibility of absorbing directly from the first excited state, was considered during this program. However, it appears more reasonable to attempt a 4-level atomic scheme in which one of the energy levels is metastable, rather than a 3-level scheme consisting of ground and first and second excited states. A little consideration shows that the first excited state never becomes sufficiently populated to produce a noticeable absorption of the modulated beam.

It is presupposed that, in a passive modulation transfer element, the majority of atoms will be in the ground state until the modulating beam is turned on; therefore, absorption of the modulating beam corresponds to ground to first excited state transitions. Now, an elementary calculation shows that the maximum number of atoms which can be made to populate the excited state at equilibrium (low-light-levels assumed) is

$$n = \tau k I_0$$

where,

n is the density of first excited atoms

τ is the natural lifetime of the excited state

k is the absorption coefficient for ground state transitions

I_0 is the intensity of the modulating beam

It should be remembered that k varies inversely with state lifetime^{66, 68} hence, assume typical values for k and τ as 5 cm^{-1} and 10^{-7} second, respectively. This gives a characteristic value for n of about $10^{-7} I_0$. Continuing in this approximate manner, a milliwatt of power should give nearly 10^{15} photons/sec-cm², with a value for n estimated at 10^8 atoms/cm³. Typical cross sections for absorption are of the order of 10^{-13} cm^2 ; hence, at

equilibrium, the absorption coefficient for the modulated beam is roughly
 $10^{-13} \times 10^8 = 10^{-5} \text{ cm}^{-1}$

certainly, too small to produce any appreciable modulation. Note that strong-ground state absorption is countered by a short lifetime, while long excited state lifetimes are countered by weak absorption, phenomena which are frequently overlooked.

If a 4-level scheme is used in which atoms in the first excited state are transferred at a rate (per atom per cc), σ_1 , to the metastable state and back to the first excited state from the metastable state at a rate (per atom per cc) σ_2 , the population of the metastable state can be estimated from elementary considerations to be

$$n_{\text{meta}} = \frac{\sigma_1 k I}{\frac{\sigma_1}{\tau'} + \frac{\sigma_2}{\tau}}$$

where k , I , and τ are as before and τ' is the lifetime of the metastable state. Here exists a possibility for a larger population, since σ_1 can potentially be made quite large.^{3, 22, 44, 66, 68} Consider the most ideal case of $\sigma_2 = 0$:

$$n_{\text{meta}} = \tau' k I$$

and the advantage of a long-lived state together with high absorption becomes realized. The depopulating effects of the two beams which are usually neglected in similar considerations have also been neglected here for the sake of clarity, but these effects will reduce the populations from the values stated without altering the validity of the arguments. Bear in mind that incident powers not exceeding milliwatts are assumed to be incident on the MIROS element.

The conclusions reached above are borne out experimentally. Attempts to observe self-reversal of spectral lines corresponding to second-to-first excited state transitions have rarely been observed, even with long discharge lamps viewed end on, and high intensity excitation methods. Spectral lines, corresponding to metastable to the fourth level state transitions, are easy to self-reverse using proper techniques.

4. SURVEY OF MATERIALS

4.1 GENERAL COMMENTS

One of the more difficult problems associated with the MIROS scheme is finding suitable materials; i. e., substances in which new optical absorption bands or lines can be produced by irradiation. The mercury system, upon irradiation with the resonance line, shows spectral absorption of all lines terminating on the 7^3P_0 level. This vanishes when the resonance line is turned off. In this case, the MIROS scheme is sensitive only when the mercury 2537A line is used as the "write" beam and the 4047A (or some other line terminating on the 7^3P_0 level) is used as the read beam. The system is so sensitive only to these two lines that the spectral width over which it responds is measured in milliangstroms.

In most cases, other spectral regions are desired. Since the mercury system cannot be made to operate in any other spectral region, a search for materials which will operate similarly to the mercury system, but in other spectral regions, is required. The most obvious beginning is with other metallic vapors.

Problems arise immediately because of the low vapor pressure of most of these metals. Cesium and rubidium absorption cells have been made, but here again the narrow spectral responses limit the system. Cadmium vapor presents an interesting possibility since the energy level structure is similar to mercury; i. e., singlets and triplets. However, the primary resonance line is the 2288 A line which in addition to the fact that cadmium requires heat to produce sufficient vapor pressure eliminates cadmium from further consideration. Sodium vapor is, of course, always considered. In this case, because its energy levels are doublets, a Kastler-Bloom pumping scheme would be required, similarly to cesium and rubidium. Vapor

pressure considerations rule out sodium. Other metallic vapors are lead and zinc. Excellent discussions of metastable lifetime and the possibility of induced absorption are given in Mitchell and Zemansky, Resonance Radiation and Excited Atoms,⁶⁶ and Peter Pringsheim, Fluorescence and Phosphorescence.⁶⁸ In brief, the search for satisfactory MIROS materials among metallic vapors does not indicate many good candidates.

4.2 ORGANIC COMPOUNDS

A number of possibilities is discovered when the search is extended to organic compounds. Normally, these substances are overlooked in fluorescence and phosphorescence applications because of their low dissociation energies, however, in a MIROS system where the incident powers are necessarily measured in milliwatts, there should be no danger of dissociation from excessive energy. Moreover, organic liquid and solid solutions respond over broad spectral ranges.

The energy levels are not as easily determined in these complex systems, so the concept of singlet, doublet, triplet, etc becomes somewhat hazy. Nevertheless, much important work has been accomplished in many compounds by assuming a close analogy to the singlet and triplet states of a mercury-like system. Such a concept has proved fruitful in determining "metastable" lifetimes through measurements of afterglow duration and factors affecting the quenching of fluorescence and phosphorescence. Jablonski⁴⁸ has given a theoretical treatment of fluorescence and phosphorescence in complete analogy to the energy level scheme of mercury: fluorescence being defined as a direct decay from some excited state to ground, and phosphorescence being defined as an indirect decay to ground; i. e., the atom in an excited state falls first to metastable, then back to excited and from there to ground, emitting the characteristic resonance line.

Lewis and his school^{40, 41, 42, 43} strengthened the analogy by numerous calculations, showing that the probable energies of metastable states agree well with values which can be derived from various considerations concerning the energy difference between the singlet and triplet states of the compounds. In the case of fluorescence, the fact that the state M is really a

triplet state has been proved by a direct method. If fluorescein dissolved in boric acid is irradiated with blue light of sufficient intensity to transfer a large fraction of molecules to the metastable state, the material becomes paramagnetic; thus the electrons have acquired a spin momentum greater than zero and probably equal to 1, corresponding to a triplet state. For further information, the reader is referred to Pringsheim's, Fluorescence and Phosphorescence.⁶⁸

That a change in the absorption spectrum of an organic compound can be induced by an exciting lamp was demonstrated by Lewis in 1941,⁴² using fluorescein dissolved in boric acid. The samples of fluorescein in boric acid used for studying the absorption spectra consisted of plates about 1 millimeter thick. Using a plate of the phosphor of known thickness and concentration, curve 1 of figure 1 was obtained by normal measuring methods. When a mercury arc was turned on, curve 2 of figure 1 was obtained. Note that the band at 4360 Å has been greatly diminished while bands at 5050 Å and 6500 Å were greatly enhanced. If the last two bands were due to the substance in the phosphorescent state, it would appear that their appearance in curve 1 must be due to the relatively feeble measuring light itself. This supposition was verified by Lewis⁴² by placing a yellow-filter between the tungsten lamp and the sample. Under these conditions the absorption at 6500 Å dropped to zero. If under the ordinary conditions of measurement some of the normal molecules were removed to the phosphorescent state, the maximum at 4360 Å of curve 1 is less than it would be for the pure normal molecules. To obtain the true height of the maximum, Lewis⁴⁰ studied it in a series of experiments in which wire screens were interposed between the tungsten lamp and the phosphor. The specific absorption rose with diminishing illumination and was extrapolated to zero illumination. Thus, curves 1 and 2 of figure 2 were obtained for the absorption coefficients of the normal and metastable state. Lewis' experiment was performed at -95° to prevent any metastable from returning to the first excited state.

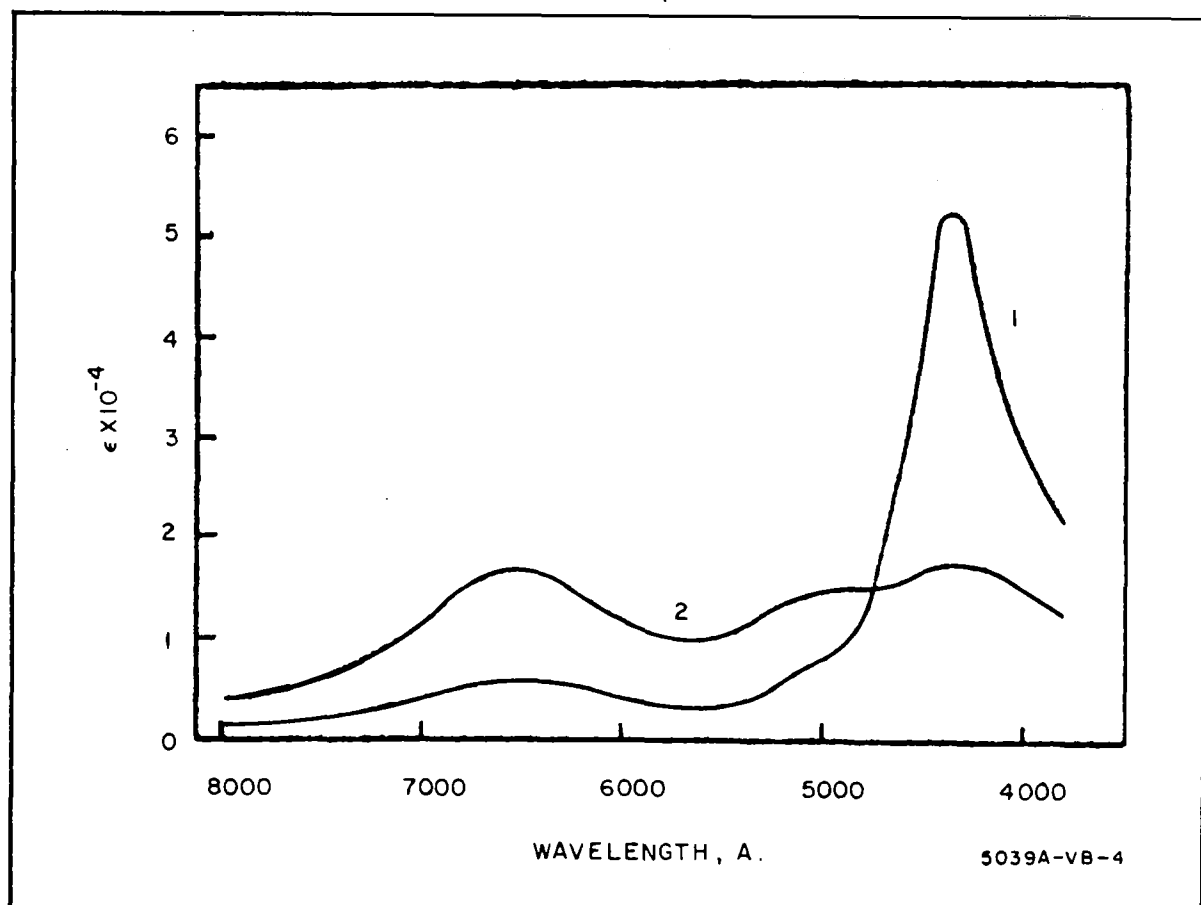


Figure 1. Absorption Spectrum of Fluorescein in Boric Acid:
 (1) Without Illumination Other Than Measuring Light;
 (2) Illumination by High Pressure Mercury Arc

Lewis was especially interested in the existence of the triplet metastable state. In a series of papers, he investigated phosphorescence and the triplet state for many organic compounds both at low and room temperatures. Table I lists some of the compounds studied by Lewis and his coworkers. This will indicate the enormous number of possibilities afforded by the organic compounds.

Linschitz and Sarkanen,²³ using flash illumination, studied in detail the absorption spectra and decay kinetics of the metastable states of chlorophyll A and B in pyridine and benzene solution at 25°C. They found the spectra

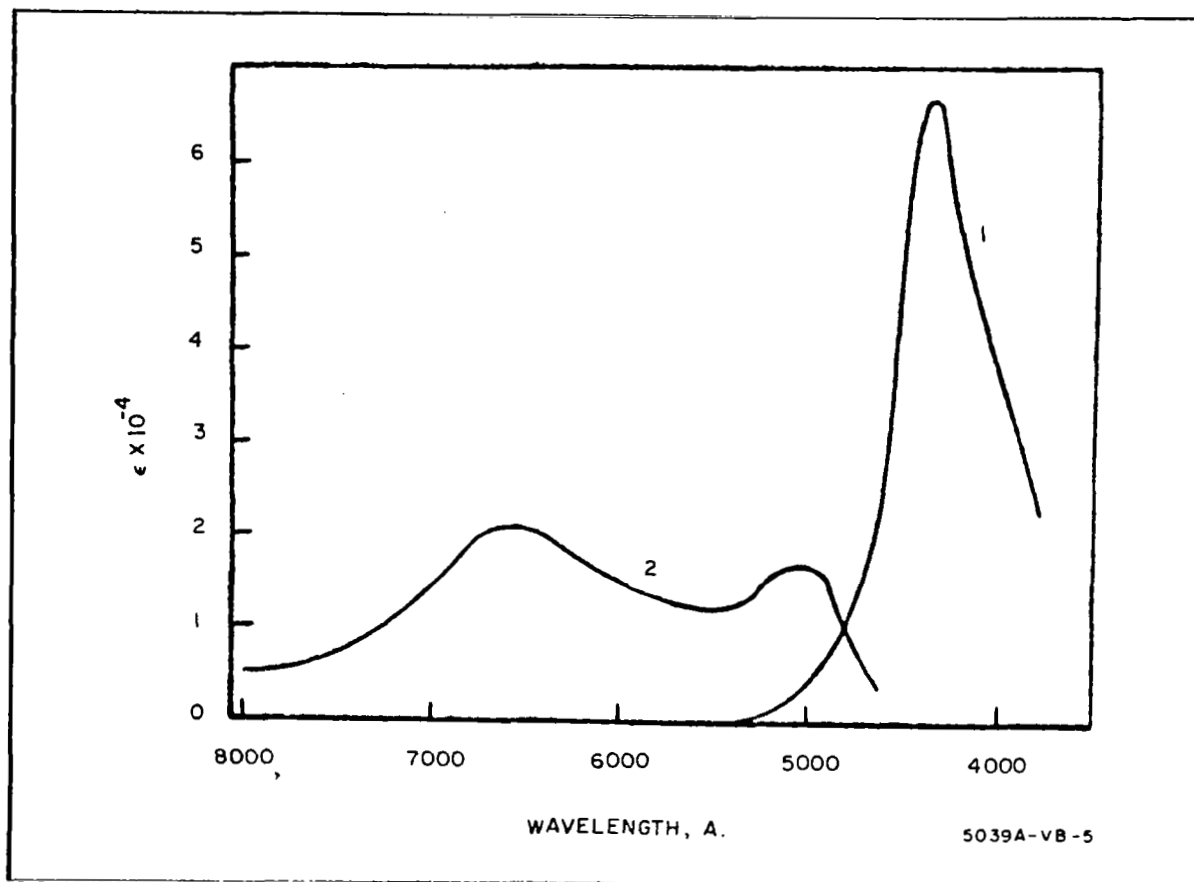


Figure 2. Molar Extinction Coefficients of Fluorescein in Boric Acid: (1) Normal (N) State; (2) Phosphorescent (P) State

particularly diffuse with measurable absorption extending beyond 7500 A. Figures 3 and 4 indicate the absorption spectra of these compounds.

Pekkarinen and Linschitz²⁶ studied the spectra and decay kinetics of tetraphenylporphine, zinc tetraphenylporphine, and bacteriochlorophyll, using flash techniques. Their results are shown in figures 5, 6, 7, and 8.

In a series of papers, Livingston and Fujimori^{24, 25} made a study of metastable absorption. Their results are shown in figures 9 through 12 and table 2, and also in table 3 and figures 13, 14, and 15.

TABLE 1
PHOSPHORESCENCE DATA

Substance	$\bar{\nu}_p, (\text{cm}^{-1})$
Ethylene Derivatives	
1 Ethylene	25000
2 sym-trans-Dichloroethylene	25300
3 sym-trans-Dibromoethylene	25200
4 sym-trans-Diodoethylene	25100
5 Lycopene (main band)	18300
6 Hexachlorobutadiene	25800
7 cis-Stilbene	21700
Hydrocarbons and Nitrogen Analogs	
8 Benzene	29800
9 Naphthalene	21300
10 Chrysene	20000
11 Anthracene	14700
12 Phenazine	15300
13 Biphenyl	22800
14 Quinoline	21700
Amines	
15 Aniline	26800
16 Diphenylamine	25200
17 Triphenylamine	24500
18 α -Naphthylamine	20100
19 β -Naphthylamine	20100
20 Dimethyl- α -naphthylamine	20300
21 Phenyl- β -naphthylamine	20200
22 Di- β -naphthylamine	19800
23 2-Amino fluorene	22700
24 Carbazole	24500
25 1, 8-Diaminonaphthalene	19100
Nitro Compounds	
26 Nitrobenzene	21100
27 α -Nitronaphthalene	19200
28 2-Nitro fluorene	20600
29 2-Nitrobiphenyl	20800
30 4-Nitrobiphenyl	20500
31 t-4-Nitrostilbene	17400
32 1, 5-Dinitronaphthalene	19900
33 1, 8-Dinitronaphthalene	20000
34 4, 4'-Dinitrobiphenyl	20200

TABLE 1 (Continued)

Substance	$\bar{\nu}_p, (\text{cm}^{-1})$
Nitro Compounds (Continued)	
35 8-Nitroquinoline	20200
36 3-Nitrodiphenylene oxide	19800
37 p-Nitroaniline	19300
38 1-Nitro-2-aminonaphthalene	19300
39 1-Nitro-5-aminonaphthalene	17900
40 m-Nitroacetophenone	20300
41 1-Nitro-2-methylantraquinone	20700
Aldehydes and Ketones	
42 Benzaldehyde	25200
43 α -Naphthaldehyde	19900
44 Acetophenone	26000
45 Benzophenone	24400
46 Thiobenzophenone	14100
47 Methyl α -naphthyl ketone	20200
48 Michler ketone	21700
49 Dibenzalacetone	18500
50 Benzil	21600
51 Biacetyl	19700
52 Acetyl propionyl	18600
53 Di-isopropyl ketone	25900
54 Anthraquinone	20400
Other Benzene Derivatives	
55 Toluene (K)	28900
56 Phenol (K)	28500
57 Benzonitrile (K)	27000
58 Benzoic acid	27200
59 p-Dichlorobenzene	26000
60 α -Methylnaphthalene	21200
61 β -Methylnaphthalene	20800
62 α -Chloronaphthalene	20700
63 β -Chloronaphthalene	21000
64 α -Bromonaphthalene	20700
65 β -Bromonaphthalene	21100
66 β -Iodonaphthalene	21040
67 α -Naphthol	20500
68 β -Naphthol	21100
69 Methyl α -naphthyl ether	20900
70 α -Naphthoic acid	20200

TABLE 1 (Continued)

Substance	$\bar{\nu}_p$, (cm ⁻¹)
Other Benzene Derivatives (Continued)	
71 β -Naphthoic acid	20900
72 Ethyl α -naphthoate	20100
73 α -Naphthonitrile	20100
74 β -Naphthonitrile	20700
75 Thio- β -naphthol	20800
Quinoline Derivatives	
76 8-Methylquinoline	21300
77 2,4-Dimethylquinoline	21800
Other Biphenyl Derivatives	
78 2,2'-Difluorobiphenyl	24400
79 4,4'-Difluorobiphenyl	23000
80 2,2'-Dichlorobiphenyl	25000
81 2,2', 6,6'-Tetrachlorobiphenyl	24500
82 2,2', 4,4', 6,6'-Hexachlorobiphenyl	23200
Miscellaneous	
83 Di- α -naphthylurea	20200
84 (Acid) Fluorescein	17700
85 Crystal violet carbinol	21300
86 Crystal violet	13600
87 Malachite green carbinol	21400
88 Eosin	14900
89 Acridine yellow	20200

Allison and Becker²² studied the effects of metal atom perturbations on the luminescent spectra of porphyrins and determined the lifetimes of many of the triplet metastable states of many of the metalloporphyrins.

The possibility of populating metastable states and thereby altering absorption spectra in organic compounds has stimulated some interest in the laser field. Sorokin, Luzzi, Lankard, and Pettit⁴⁴ studied Q-switching a ruby laser by placing a 3- or 5-centimeter absorption cell, containing either the free base, chloroaluminum or vanadium phthalocyanines diluted in either chloronaphthalene or nitrobenzene, between an uncoated ruby laser crystal polished with a totally internally reflecting rooftop on one end and a multiple

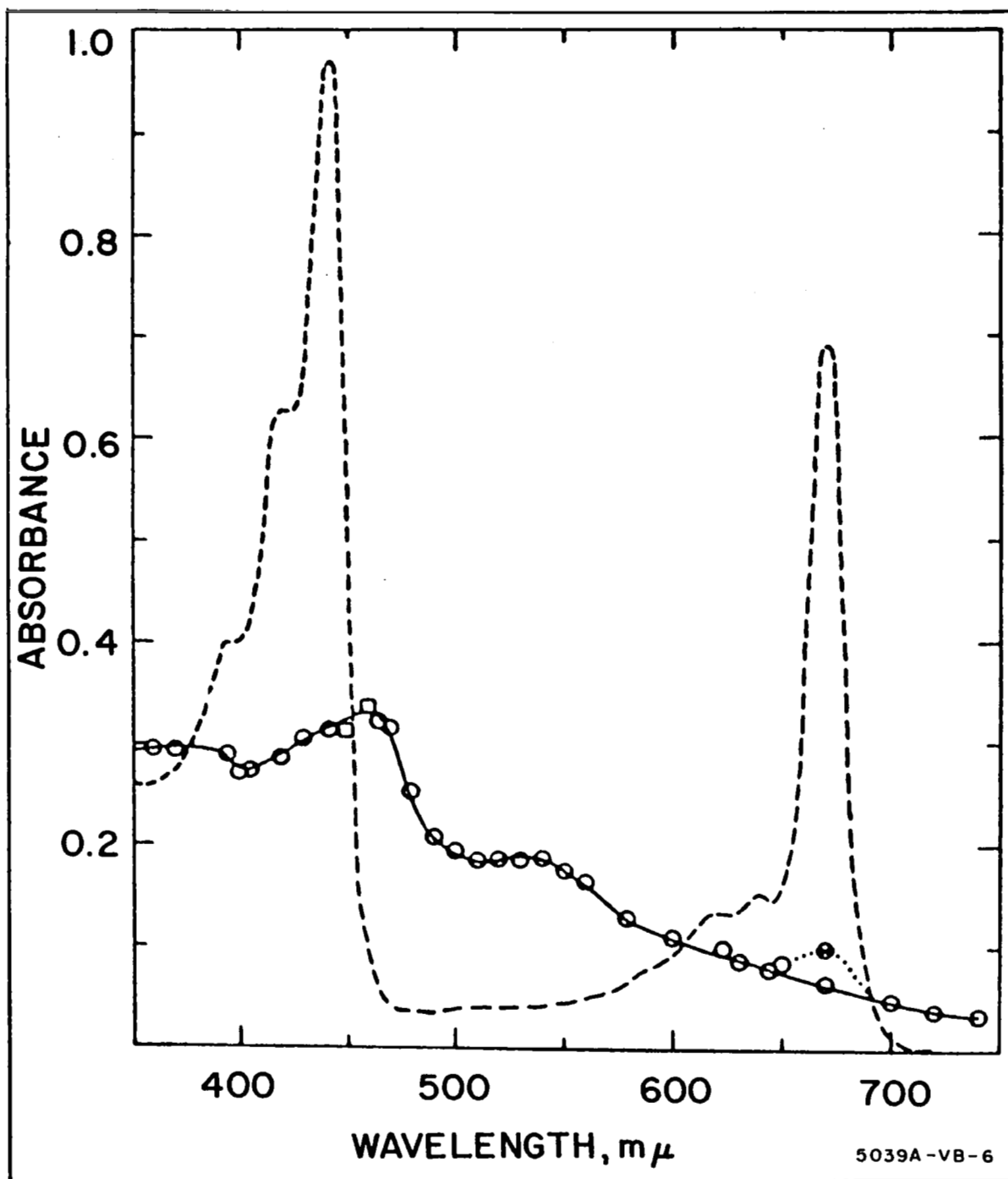


Figure 3. Absorption Spectra of Chlorophyll A and its Metastable State, in Pyridine; 2.1×10^{-6} M; Cell Length, 5 cm; ○, Corrected Spectrum, Using Relative Calibration of Oscillograph Deflection, □, Corrected Spectrum, Using Absolute (Natural Screen) Calibration; ●, Original Uncorrected Absorbance, Immediately After Flash

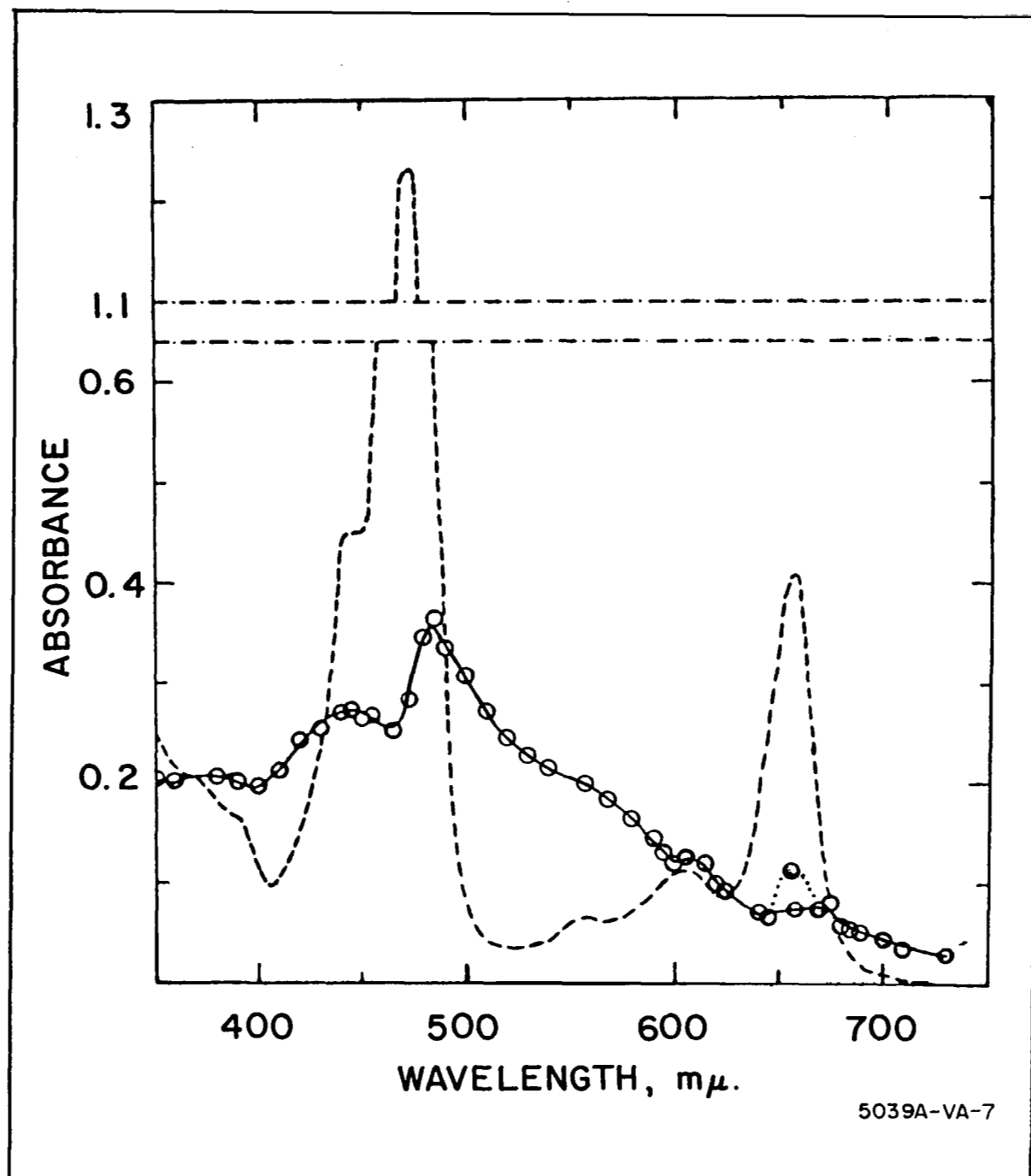


Figure 4. Absorption Spectra of Chlorophyll B and its Metastable State, in Pyridine; 2.1×10^{-6} M; Cell Length, 5 cm: O, Spectrum Corrected to 100% Conversion, ●, Original Uncorrected Absorbance, Immediately After Flash

TABLE 2
SUMMARY OF SPECTRAL DATA FOR THE COMPOUNDS
IN THEIR METASTABLE STATES

Compound	Solvent	$m \times 10^6$ (moles/l)	Maxima (m μ)	$\Delta\lambda$ (m μ)	Max % of trip- let	$\tau \ 1/2 \times 10^6$ (sec)	Order	k(1st order) (mole ⁻¹ sec ⁻¹ total pigment concn)
Chlorophyll-A	Benzene	1.5	460	28	72	150 \pm 25%	1st(?)	3×10^9
Chlorophyll-A	Methanol	1.1	462, 425(?) 390(?)	28	90	200 \pm 25%	?	3×10^9
Chlorophyll-A	Cyclohexanol	1.0	465, 360	30	95	600 \pm 30%	?	1×10^9
Chlorophyll-B	Benzene	1.0	482, 440 420(?)	22	90	1300 \pm 25%	1st	5×10^8
Chlorophyll-B	Benzene	2.2	485	21	90	600 \pm 30%	1st	5×10^8
Chlorophyll-B	Benzene	9.2	485, 430	23	75	200 \pm 30%	1st	4×10^8
Chlorophyll-B	Methanol	3.5	496, 454 420(?), 390(?)	29	80	100 \pm 40%	?	2×10^9
Pheophytin-A	Benzene	2.5	480	-	-	-	-	-
Porphyrin	Benzene	5	390, 423	17	80	250 \pm 50%	?	5×10^8

TABLE 3
ABSORPTION MAXIMA CORRESPONDING TO THE TRIPLET STATES

Compound	Solvent	Conversion (%)	Abs max,* (mμ)	Range of λ's Studied, (mμ)
Chlorophyll-A	Benzene(wet)	85	(440?), 465	410-750
Chlorophyll-A	Benzene(dry)	60	450?	410-750
Chlorophyll-A	Methanol	80	450, (550?)	420-660
Chlorophyll-A	Pyridine	85	460	380-740
Chlorophyll-A	Pyridine	95	(370), 462, (530)	380-740
Chlorophyll-AB	Benzene(wet)	80	430?, 480	420-680
Chlorophyll-B	Benzene(dry)	65	440?, 475, (580?)	420-690
Chlorophyll-B	Pyridine	90	480	380-740
Chlorophyll-B	Pyridine	90	(445), 485, (550) (605)	380-730
Pheophytin-A	Benzene(wet)	75	430?, 500	420-690
Pheophytin-A	Pyridine	75	430?	420-690
Pheophytin-B	Benzene(wet)	75	430?, 460, (510)	420-690
Pheophytin-B	Pyridine	75	410?, 460, (520?)	380-690
Zn-Chlorophyll-A	Benzene(wet)	70	450	420-750
Zn-Protoporphyrin	Methanol	75	455	430-670
Protoporphyrin	Methanol	60	440, (530?)	430-680
Protoporphyrin	Pyridine	60	350, 420	350-680
Mesoporphyrin	Pyridine	60	450	440-680
Tetraphenylchlorin	Benzene(wet)	80	470, 520?	450-690
Mg-Phthalocyanine	Pyridine	65	400, 470	380-710

* Parentheses indicates that the wave lengths correspond to minor absorption bands; question marks, that the observed maxima are of doubtful significance.

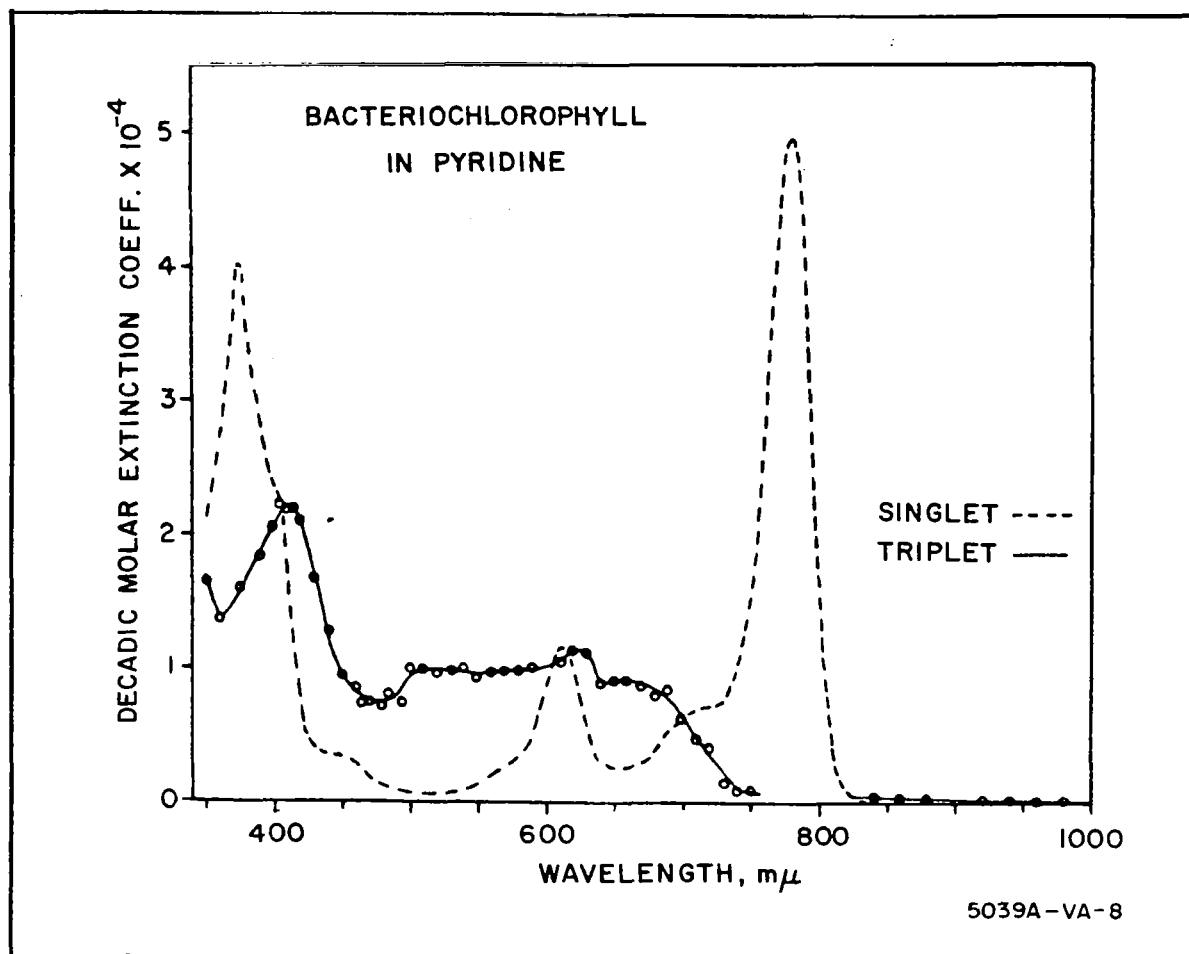


Figure 5. Absorption Spectra of Bacteriochlorophyll (Dashed Line) and its Triplet State (Solid Line), Corrected to 100% Conversion, in Pyridine

dielectric mirror reflecting 99 percent at 6943 Å. The concentrations of the phthalocyanine solutions in the order of 10^{-6} M were adjusted to transmit 50 percent at 6943 Å at low levels in a single pass-through cell. The ruby laser was then pumped to the point where it should normally have started to lase. Instead, a giant pulse occurred which appeared to have no more than a nanosecond width in the cases of the chloroaluminum and vanadium solutions. In all cases, the giant pulses were as intense as any obtained with rotating

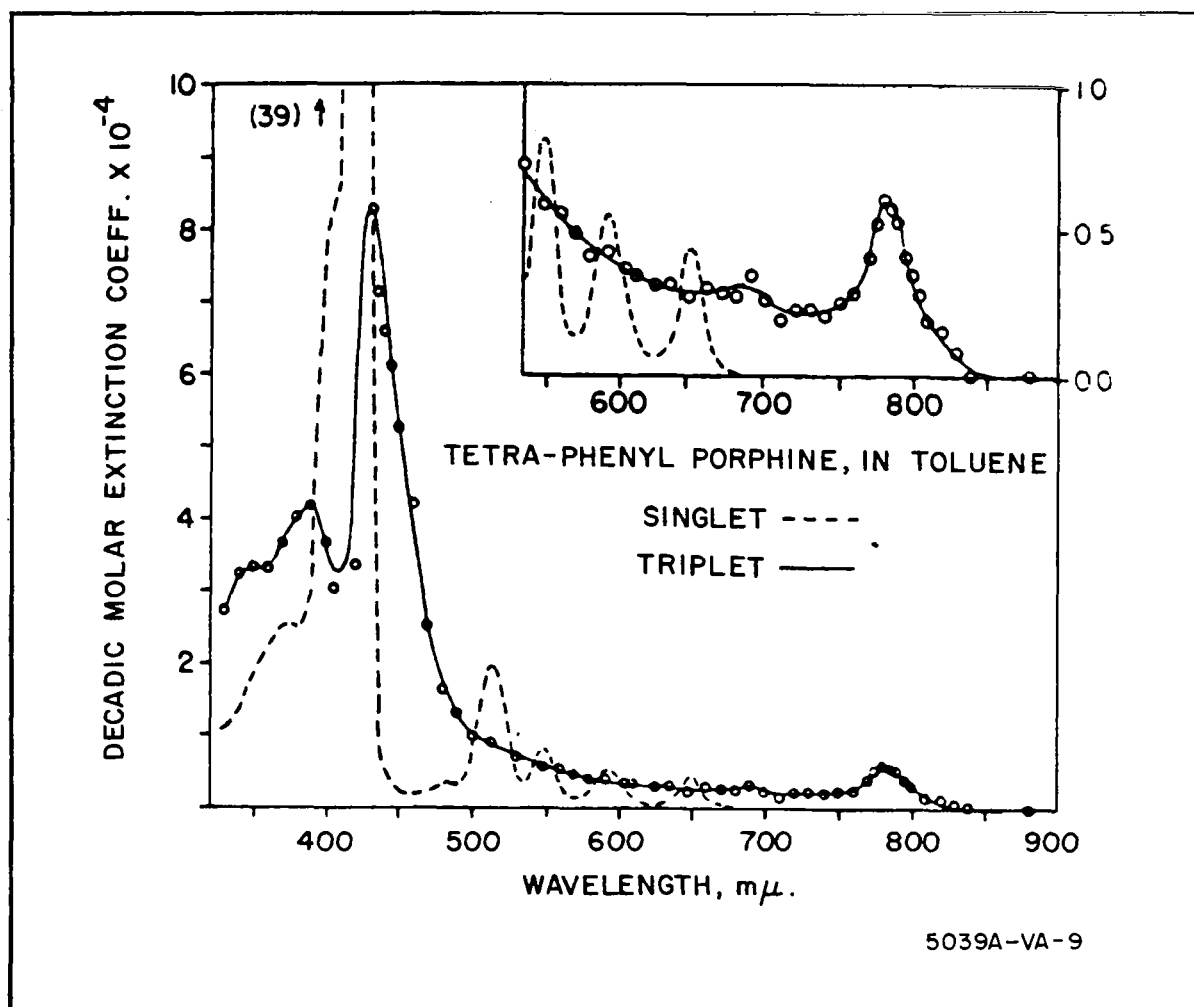


Figure 6. Absorption Spectra of Tetraphenylporphine (Dashed Line) and its Triplet State (Solid Line), Corrected to 100% Conversion, in Toluene

prisms for Q-switches. They speculated that the bleaching which occurs during the first giant pulse mainly represents saturation of the singlet-singlet transitions.

The population rate, k'_{sT} has been estimated in a paper by Gurinovich, Sevchenko, and Solov'ev³ to be approximately $1.3 \times 10^{-7} \text{ sec}^{-1}$. In their paper, they noted that in the metalloporphyrins, a metal ion facilitates the transition of the molecule to the triplet state. According to their paper, the

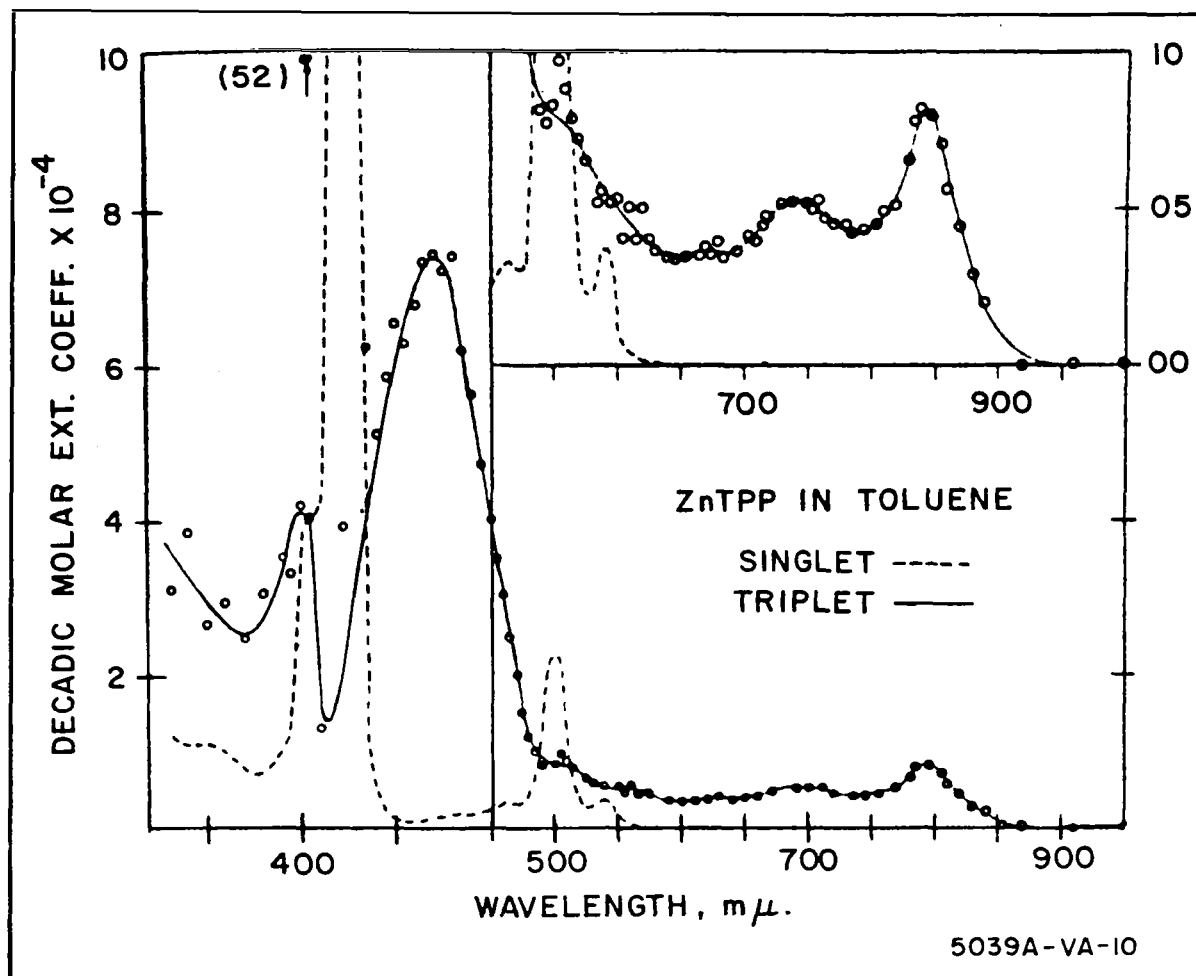


Figure 7. Absorption Spectra of Zinc Tetraphenylporphine (Dashed Line) and its Triplet State (Solid Line), Corrected to 100% Conversion, in Toluene. Note Change in Wavelength Scale at 500 mμ

introduction into an organic molecule of a heavy or paramagnetic atom (e. g., the copper ion has one unpaired electron and a large nuclear mass) results in mixing of the wave functions of the singlet and triplet states. Hence, it increases the probability of singlet-to-triplet transitions; i. e., removes the rule forbidding intercombination. For further information, the reader is referred to their paper.

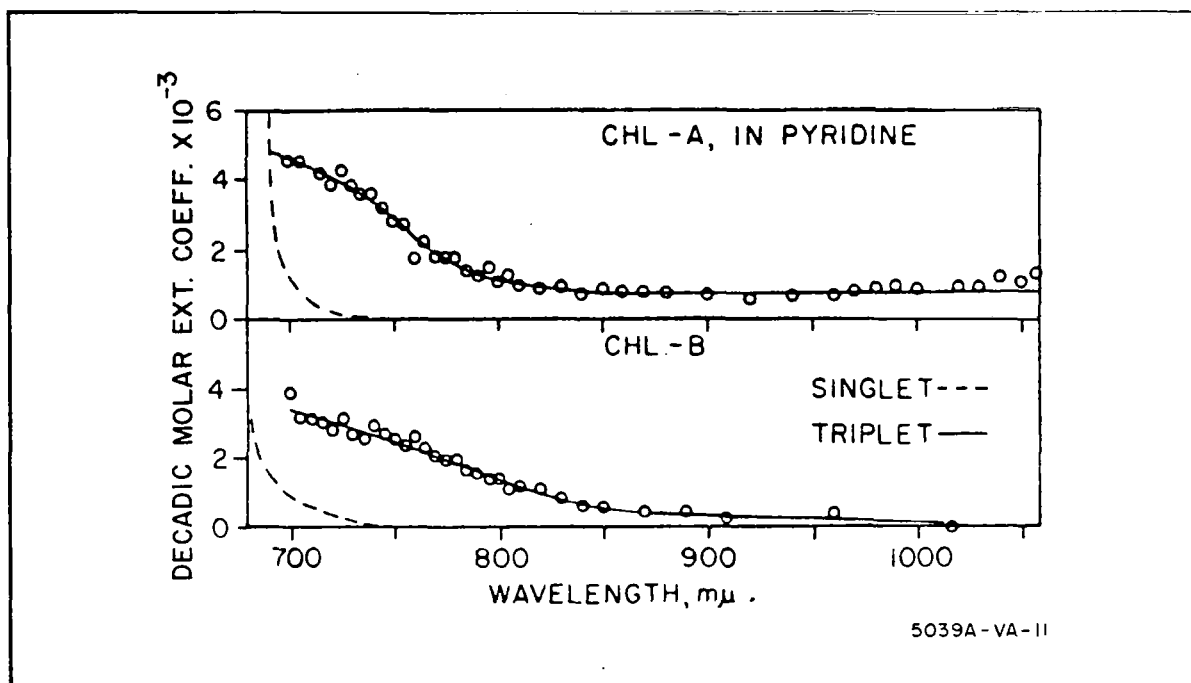


Figure 8. Near Infrared Absorption Spectra of Triplet States (Solid Lines) of Chlorophyll A (Upper Curve) and B (Lower Curve), in Pyridine

Evidently, the information available on absorption processes and metastable energy levels is voluminous. It should be apparent at this point that practically any spectral region can be matched for a suitable choice of organic materials. For more information, the reader is referred to the bibliography.

4.3 URANYL COMPOUNDS

Another class of materials which was considered is the uranyl compounds. These compounds have long been of interest in spectroscopy. Fluorescence of uranium salts has been the subject of investigation since the days of Stokes and E. Becquerel in the middle of the nineteenth century. Although it led indirectly to the discovery of radioactivity, the fluorescence of uranium salts is in no way connected with their radioactive properties. On the other hand, photoluminescence is not a property of all uranium salts, but only of uranyl compounds in which the metal is hexavalent and occurs as the ion UO_2^{++} .

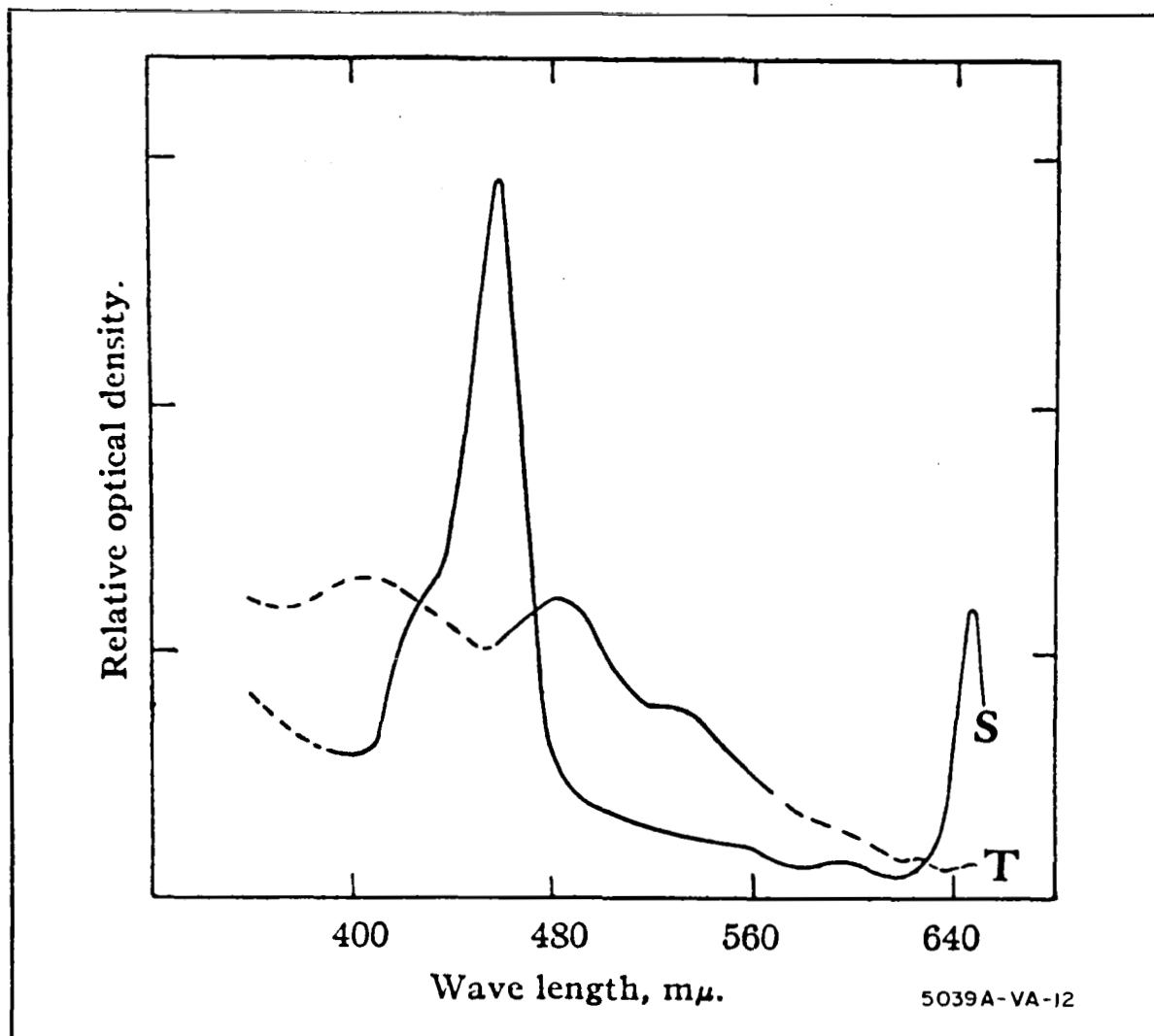


Figure 9. Absorption Spectra of Chlorophyll B in Benzene;
A Composite of Several Plots: S, Ground State;
T, Lowest Triplet State

All uranyl salts have absorption and emission spectra of the same type, differing only in detail; similar spectra are also exhibited by liquid solutions of uranyl salts. Even in solids such as sodium fluoride or calcium fluoride containing uranyl at a concentration of 10^{-6} molar, fluorescence of the same character can be excited.

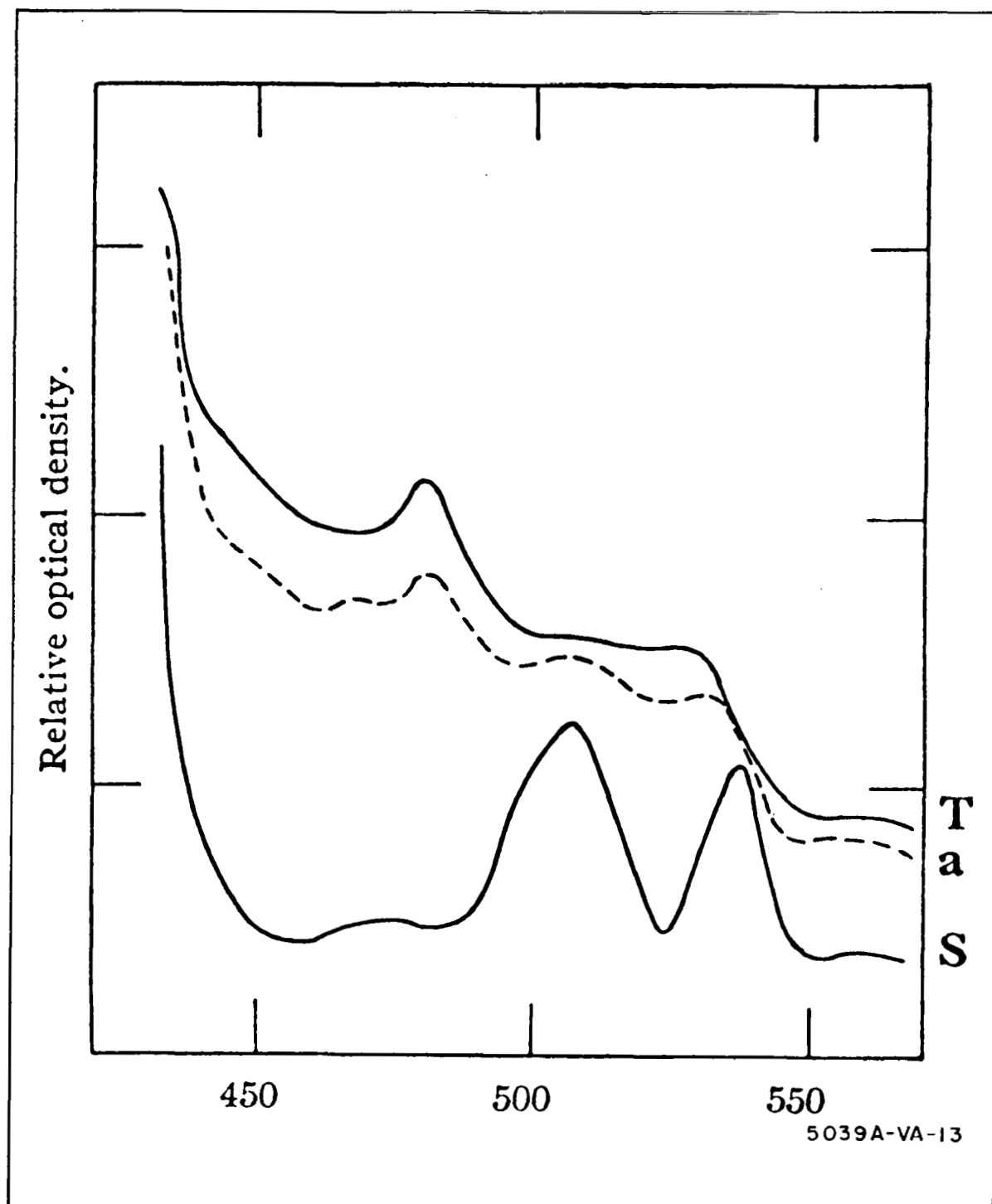


Figure 10. Absorption Spectra (2.5×10^{-6} M) Pheophytin A in Benzene: S, Ground State; a, "Immediately" After Flash; T, Lowest Triplet State

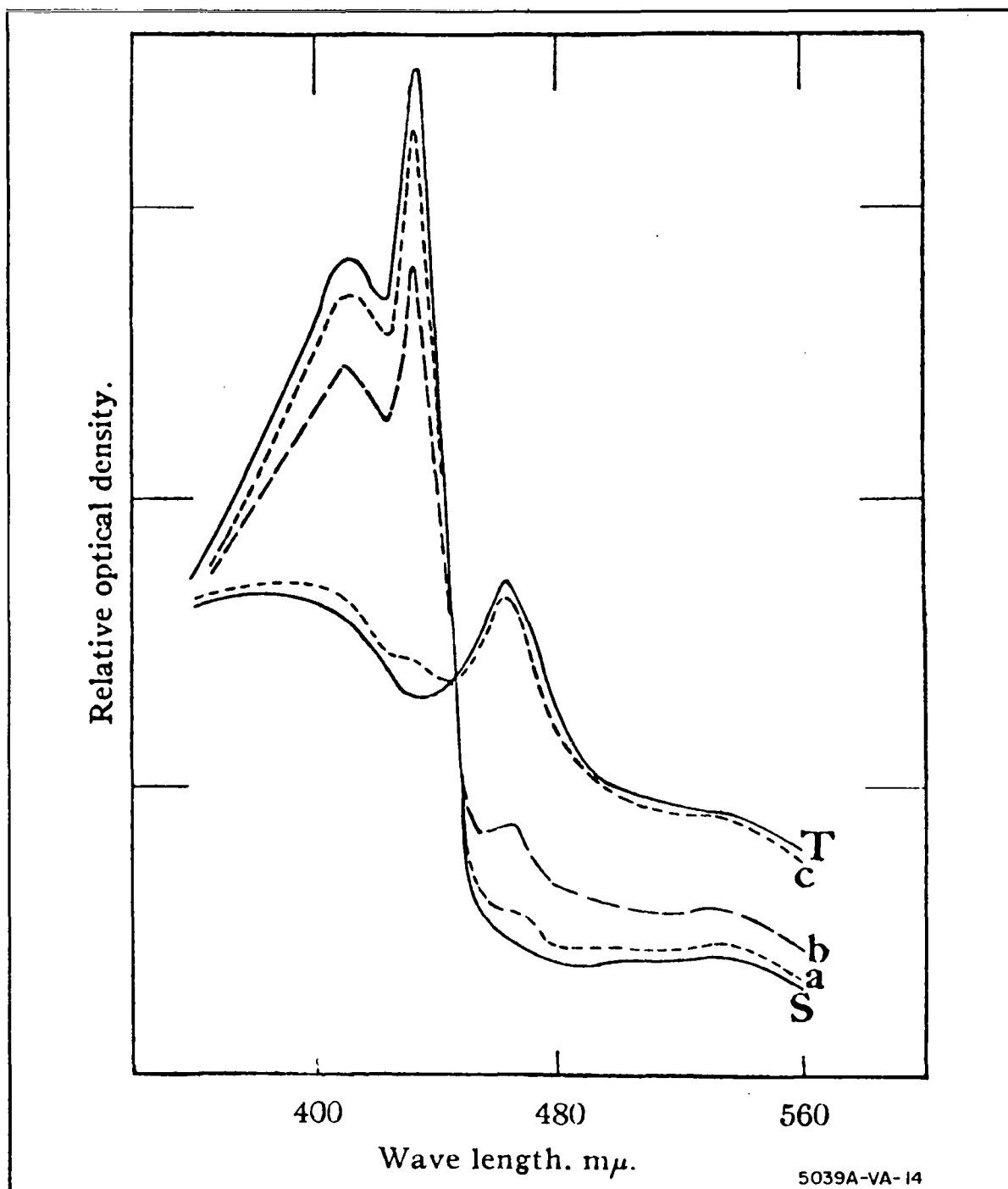


Figure 11. Absorption Spectra of (1×10^{-6} M) Chlorophyll A in Cyclohexanol: S, Ground State; a, 2600 μ sec After Flash; b, 900 μ sec After Flash; c, "Immediately" After Flash; T, Lowest Triplet State

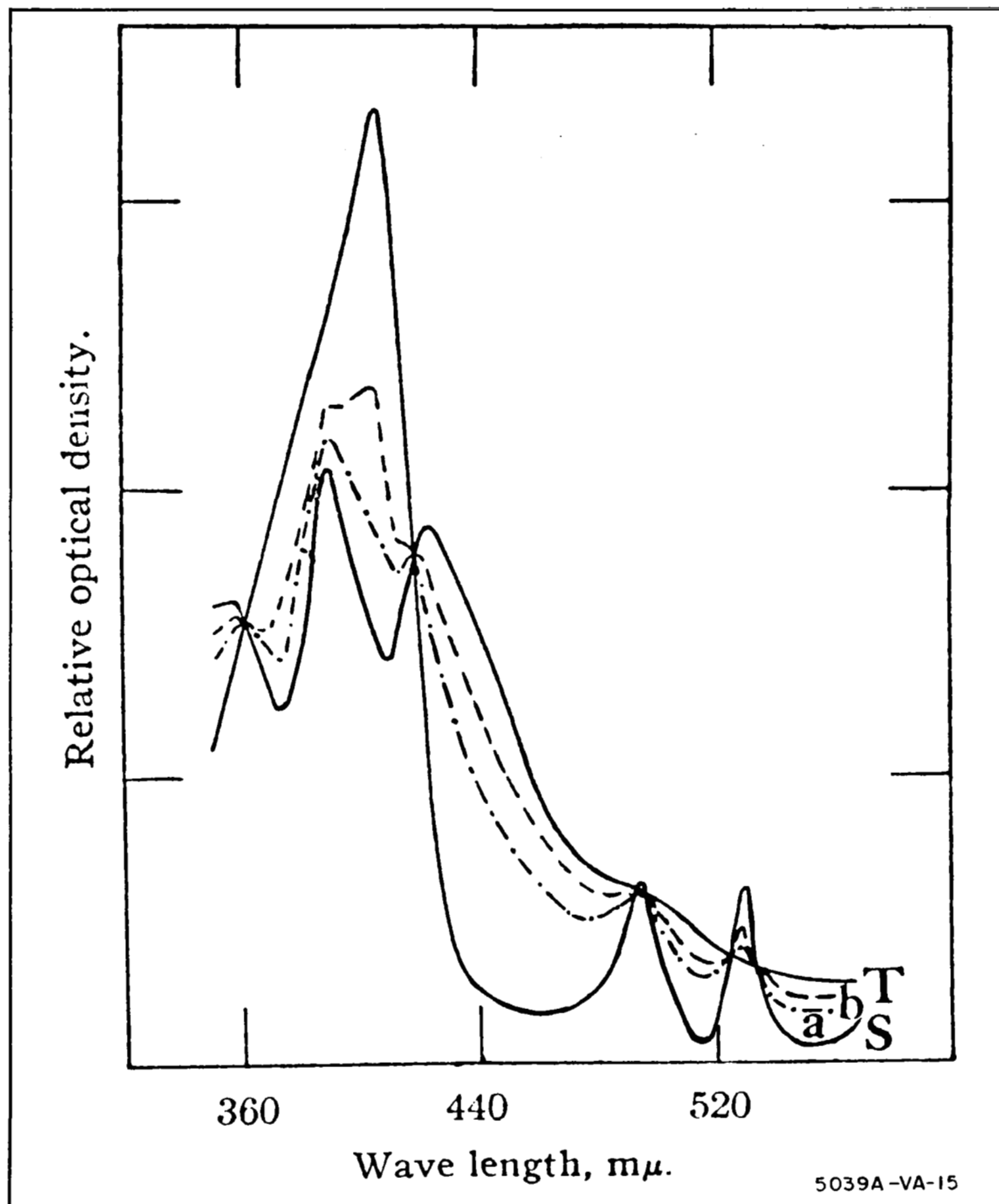


Figure 12. Absorption Spectra of Corprotophyrin Dimethyl Ester in Benzene: S, Ground State; a, 120 μ sec After Flash; b, "Immediately" After Flash; T, Lowest Triplet State

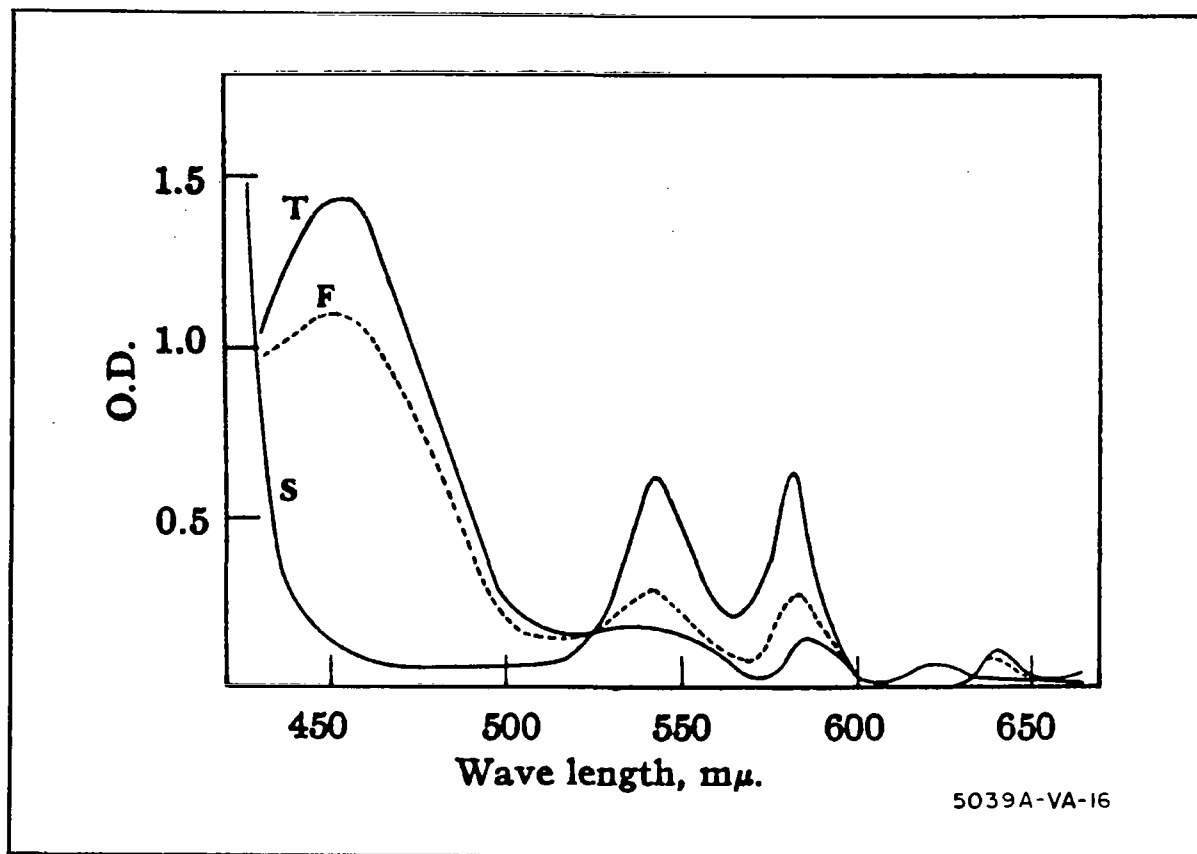


Figure 13. Absorption Spectra of Zn-Protoporphyrin: S, Absorption Spectrum of the Ground State; F, Absorption Spectrum Observed Immediately After Photolytic Flash; T, Absorption Spectrum Estimated for the Triplet State

Hiriyama and Melamed of the Westinghouse Research Laboratories studied the possibility of Q-switching a laser by doping a piece of barium crown glass with UO_2^{++} , as well as Nd^{+++} . They expected that the pump light would not only create the necessary population inversion for Nd^{+++} laser action, but that the blue and ultraviolet components of the pump lamp would excite the UO_2^{++} ions to higher electronic states, from which they could absorb the laser emission until bleached.

According to Hiriyama and Melamed, the state from which induced absorption occurs is the excited state (which is really a complex of states) from

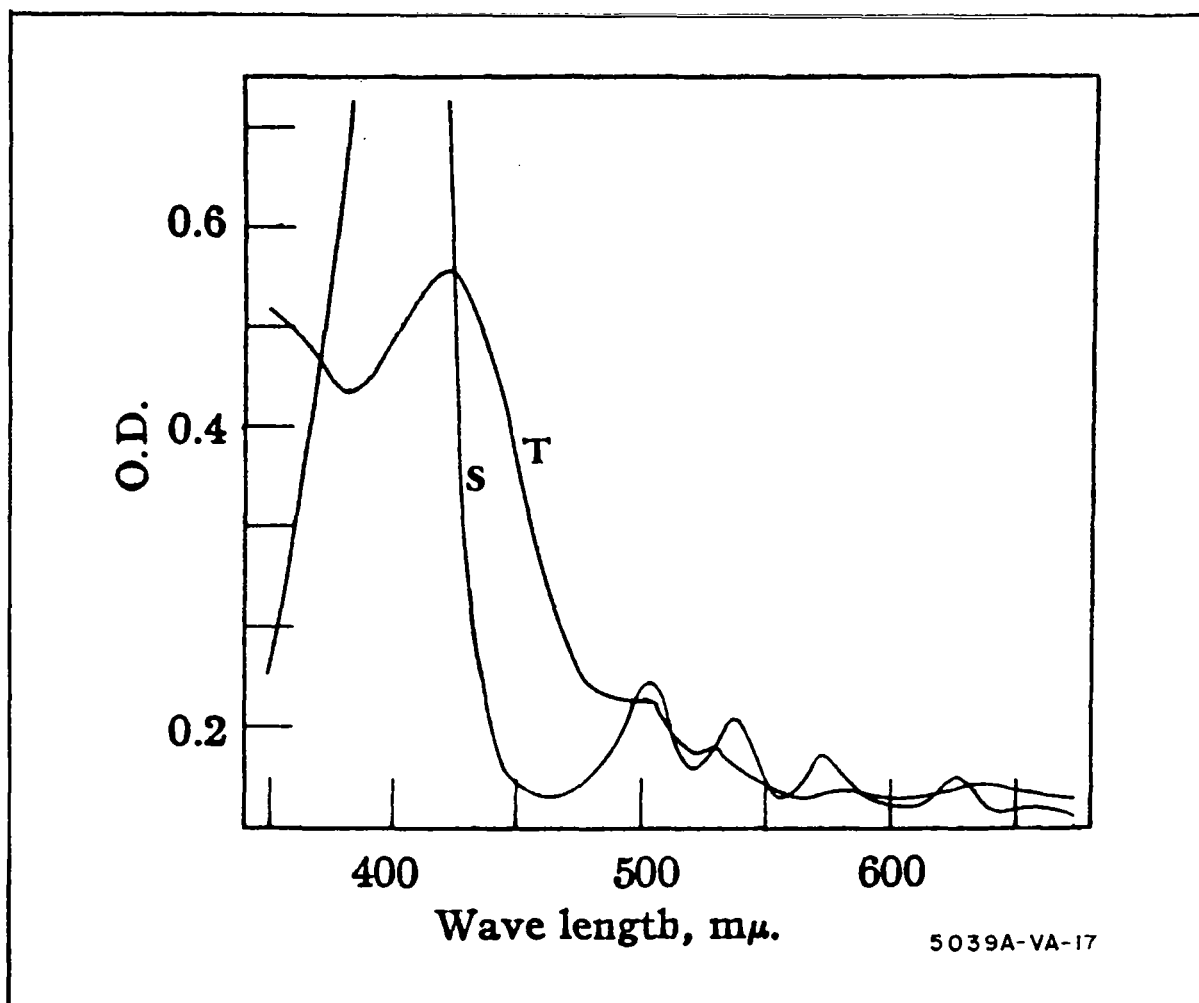


Figure 14. Absorption Spectra for Protoporphyrin: S, Absorption Spectrum of the Ground State; T, Absorption Spectrum Estimated for the Triplet State

which visible fluorescence occurs. The uranyl ion does not exhibit phosphorescence.^{55, 63, 65, 68} The strength of this induced absorption depends, among other things, on the lifetime of this first excited state. Once in the excited state, the induced absorption band extends from at least 5000 Å to 7000 Å. Bleaching occurs when the excited atom returns to ground.

Considering these facts, a very brief experiment was attempted on the MIROS system. A quartz absorption cell with flat end windows was filled with

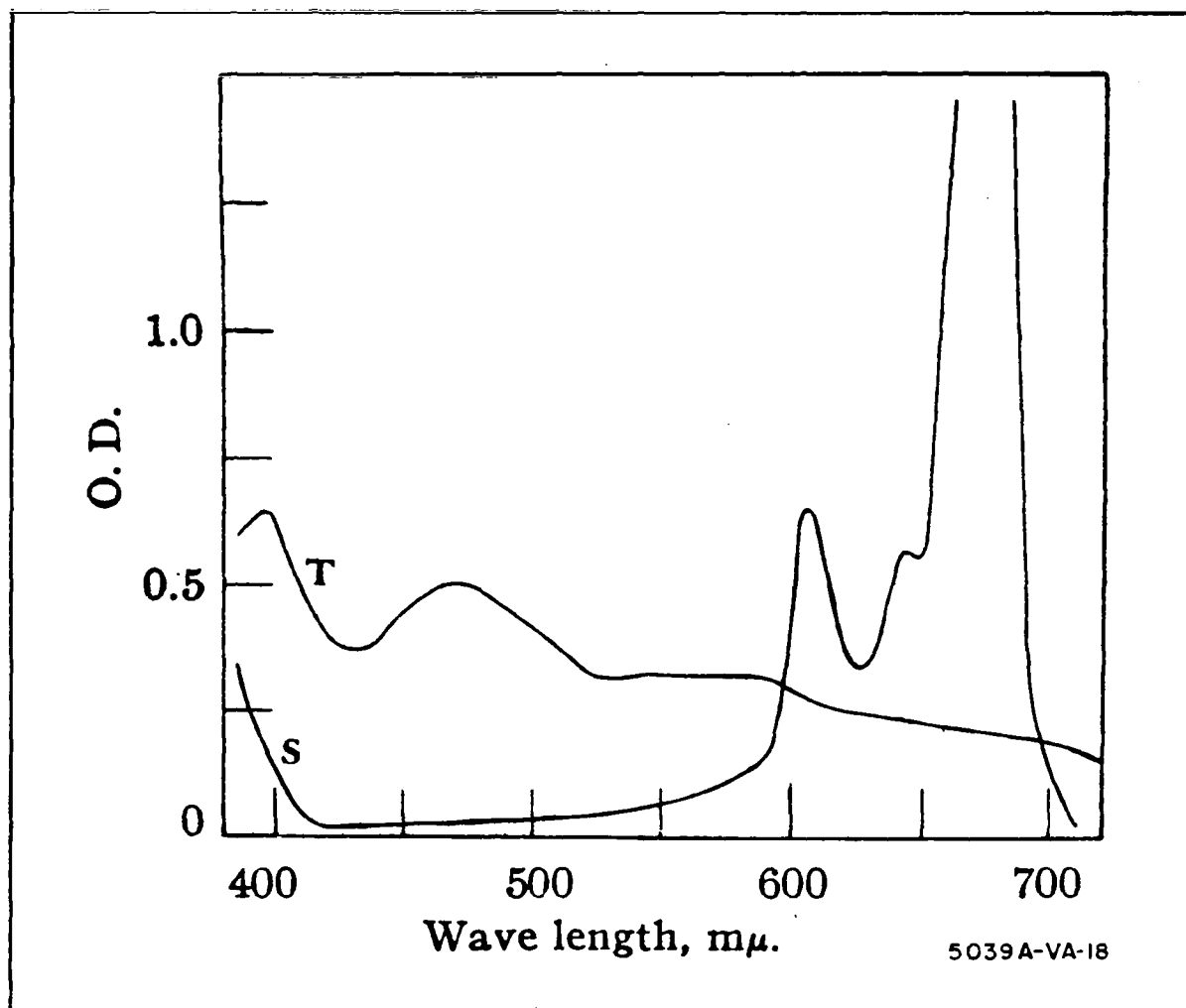


Figure 15. Absorption Spectra for Mg-Phthalocyanine: S, Absorption Spectrum of the Ground State; T, Absorption Spectrum Estimated for the Triplet State

a saturated solution of uranyl nitrate in water. This cell was placed in the path of the "read" beam, which was set at 7000 Å. While monitoring the "read" beam, a mercury penlight was held just in front of the absorption cell. Attempts were thus made to modulate the absorption of the "read" beam. These crude experiments were unsuccessful. . Even though the solution evidenced a high degree of fluorescence, no "read" beam absorption

could be induced. Indications were that insufficient power for induced modulation could be obtained from the mercury penlamp.

5. PASSIVE MODULATION BY FREE- CHARGE CARRIERS

Another method of amplitude modulating a beam of light is to introduce free-charge carriers into the path of the "read" beam. An elementary theory of absorption by free-charge carriers is easily obtained by considering a charge (usually equal to an electronic charge) with mass, m , acted on by a damping force and a sinusoidal electrical field. Its motion is given by

$$m\ddot{r} + mg \dot{x} = q E e^{i\omega t}$$

If there are N such carriers per unit volume, this equation can be written in terms of the dipole moment per unit volume by multiplying both sides of the equation by Nq .

Solving for the steady-state dipole movement per unit volume and relating this to the index of refraction, $(n-ik)$, the real and imaginary parts can be found from the relations

$$n^2 - k^2 - \epsilon = - \frac{Ne^2/m\epsilon_0}{\omega^2 + g^2}$$

$$2nkw = \frac{gNe^2/m\epsilon_0}{\omega^2 + g^2}$$

Since the absorption coefficient is proportional to the imaginary part of the index of refraction, it is evident that the absorption coefficient should vary as the density of carriers and as the square of the wavelength.

Continuing along these lines, an absorption constant for a system of free-charges, such as exists in a semiconductor, can be obtained; i.e.,

$$K = \frac{\lambda^2 e^3}{4\pi^2 c^3 n \epsilon_0} \left\{ \frac{N_n}{m_n^2 \mu_n} + \frac{N_p}{m_p^2 \mu_p} \right\}$$

where,

K is the absorption constant

λ is the wavelength

c is the velocity of light

n is the index of refraction

ϵ_0 is the free-space dielectric constant

e is the electronic charge

N_n is the density of negative free-charge carriers

m_n is the effective mass of negative free-charge carriers

μ_n is the mobility of negative free-charge carriers

N_p is the density of positive free-charge carriers

m_p is the effective mass of positive free-charge carriers

μ_p is the mobility of positive free-charge carriers

This equation was used by Gibson to measure and interpret absorption in germanium at millimeter wavelengths.

Consideration reveals that free-charge carrier absorption differs from the more familiar atomic and molecular absorption in one fundamental point; namely, there are no resonances in free-charge carrier absorption, only a steady λ^2 dependence. It is expected therefore that free-charge carrier absorption would be most effective at larger wavelengths. This is observed in practice as can be seen by reference to figure 16 for InSb.

The possibility of injected carrier absorption has been studied by A.F. Gibson⁵⁸ and R.B. McQuistan, and J.W. Schulz⁵⁷, and subsequently practical infrared modulation systems have been constructed. These, however, are not passive systems since the injected carriers are obtained by auxiliary power supplies, not optical irradiation. An entirely passive free-carrier modulation scheme has been demonstrated by Lawrence and Gibson.⁵⁸ Light of wavelength greater than 1.8μ was used to detect the presence of charge carriers in germanium. Light of wavelength less than 1.8μ was used

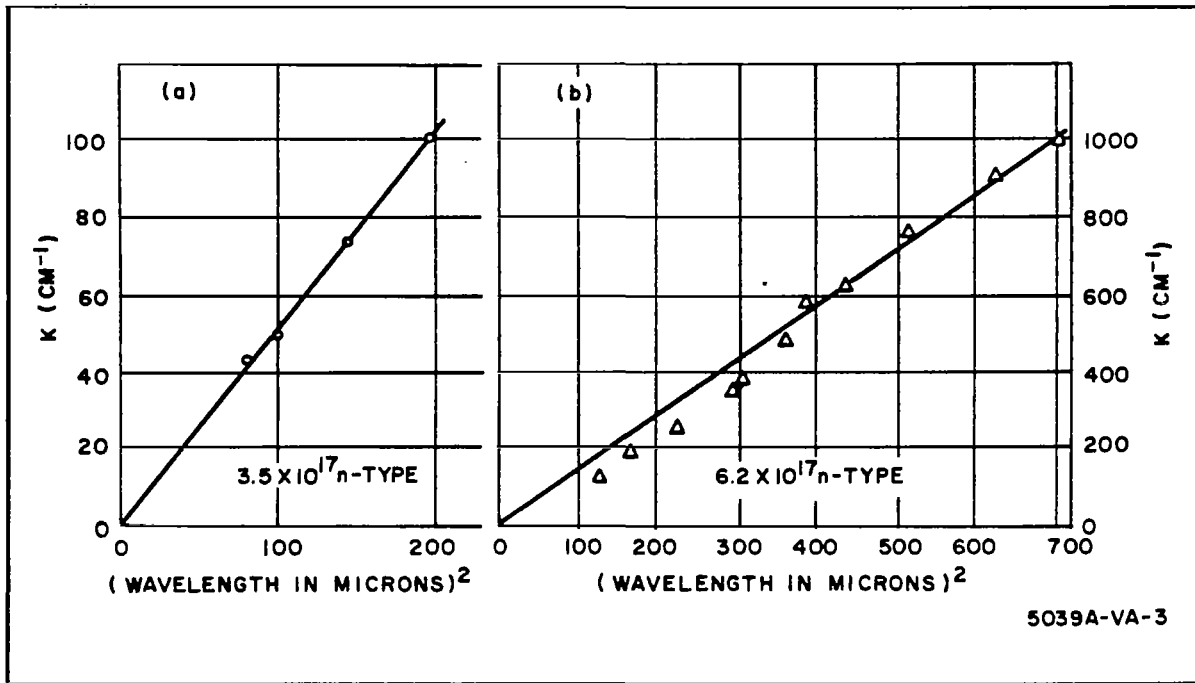


Figure 16. Wavelength Dependence of Free-Carrier Absorption in InSb

to generate the free-charge carriers. Other materials suggested by Gibson were PbS ($\lambda > 3 \mu$), Si ($\lambda > 1.2 \mu$), and SiC ($\lambda > 0.45 \mu$); however, these materials required further study at the time of Gibson's paper.

An interesting group of materials consists of the chalcogenides of zinc, cadmium, and mercury. The apparent quantum efficiency in most of these materials, for instance, can be made much larger than unity. This is explained by Moss as due to the fact that when an electron-hole pair is formed, the hole is rapidly trapped while the electron passes freely through the crystal. As the electron leaves the crystal at the anode, another enters at the cathode, and so on until the electron family recombines with the trapped hole. Gains have been reported in the region of 10^3 for ZnO, and up to 10^4 for CdS. This may not necessarily help the passive modulation scheme since the actual carrier density is not increased. In addition to change in conductance on

illumination, both ZnO and ZnS show a change in the dielectric constant on illumination (Roux, 1956; Borissou, and Kanev, 1955). This is reasonable because of the obvious interrelation between the real and imaginary parts of the complex dielectric constant. Characteristic photoconductive wavelengths for this group are shown in table 4. The latest most related, application of these compounds is laser Q-switching. Bret and Gires⁴⁶ used CdS:Se glasses, whose transmission coefficient varies from 10^{-6} to 3×10^{-1} in about a nanosecond, to Q-switch a ruby laser. They were able to build amplifier units made of a ruby rod 10 centimeters long and a glass plate with $T_o = 10$ percent with the following characteristics: low-level attenuation, high-level gain. They did not attempt to optimize their parameters and concluded that it was possible to improve their results considerably. In this application, it is not necessarily free carriers which were responsible for absorption and absorption changes; nevertheless, it seemed appropriate to include this application in this section.

TABLE 4
CHARACTERISTIC PHOTOCONDUCTIVE WAVELENGTHS

	μ	Reference
ZnO	Peak 0.4	Mollwo and Stockman, 1948
ZnO	$\lambda_{1/2}$ 0.39	Weiss, 1952
HgO	0.55	Dechene, 1939
ZnS	Peak 0.337	Piper, 1953
CdS	Peak 0.50	Bube, 1953
CdS	$\lambda_{1/2}$ 0.515	Bube, 1953
HgS	Peak 0.63	Shneider, 1956
HgS	$\lambda_{1/2}$ 0.57	Bergman and Hansler, 1936
ZnSe	Peak 0.48	Bube, 1955b
CdSe	Peak 0.725	Bube, 1955b
CdSe	$\lambda_{1/2}$ 0.78	Treu, 1939
ZnTe	Peak 0.8	Braithwaite, 1951
CdTe	Peak 0.88	Bube, 1955b
HgTe	$> 8 \mu$	Lawson, etc, 1959

From the above discussion, it is evident that light can be passively modulated by light by the mechanism of producing free-charge carriers. Because of the wavelength square dependence, the "read" beam should be in the longer wavelength region; while the write beam, in order to overcome band gap energies, must be in the visible or near infrared optical regions. Although such modulation has been observed, more research would be necessary to demonstrate practicality.

6. ALKALI HALIDES

6.1 DISCUSSION

An F-center in an alkali-halide crystal occurs as a result of the absence of a negative halide ion. This absence appears as a positive charge around which an electron can orbit. This bound electron-hole system gives rise to a series of absorption bands and the crystal appears colored; hence, the name color centers. With sufficient energy, the electron can be ionized from the vacancy, and thus be able to move freely through the crystal. The crystal then becomes conducting. It is well known that light incident on an alkali-halide crystal can cause a photocurrent to flow. Once ionized, the electron seems to prefer another F-center to a negative ion vacancy, and thus an F' -center is born. This, of course, consists of a negative ion vacancy around which two electrons orbit. The energy levels are higher than F-center levels, so F' -absorption bands occur at wavelengths several thousand angstroms longer than F-absorption bands.

The fact that a new absorption band could be created upon irradiation of an alkali-halide crystal with light corresponding to its F-absorption band was demonstrated as early as the thirties by Pohl and Pick.⁶⁹ It was also shown that the photoionization current varied rapidly with incident F-light although the effect was temperature dependent. It was further demonstrated that an equilibrium condition could be setup between F- and F' -centers, during which a flash of light could cause a rapid change in optical density of the crystal.^{59,60}

Considering these facts, it seemed reasonable to try an experiment, in addition to the mercury cell experiment, in which attempts would be made to modulate rapidly the optical density of an alkali-halide crystal by irradiating it with F- and F' -light. Two particular alkali halides were studied, KCl and KI, even though very little information on KI F- and F' -centers is available. The following is a discussion of the experimental results.

6.2 EXPERIMENT

Crystals of optical quality of KI and KCl were acquired from Harshaw Chemical Company. Samples were cleaved from these larger crystals with dimensions of approximately 1/2- by 1/2- by 3/16-inch. One group of these crystals had been irradiated six months before, using 300 kev electrons for 2.5 hours with a total accumulated charge of 25 to 40,000 microcoulombs. These samples were wrapped in 0.5-mil aluminum foil and retained in them during and after irradiation. Wrapped in this manner, they were stored in a desiccator for the aforementioned period of time until used. These were examined in room light and found to have bleached in that period of time. Samples were then sent to the radiation laboratory and irradiated at 2 mev until heavily colored. These samples were also wrapped in 0.5-mil aluminum foil and stored in a desiccator.

Using an evacuated dewar with a realizable vacuum of 10^{-6} millimeter of mercury, the samples were examined at room and liquid nitrogen temperatures to determine what absorption bands were present and their characteristics. Using the Carey 14 spectrophotometer, KI crystals treated in this manner indicated F- and F'-bands at 6943 and 11,000 Å respectively. These measurements yielded an optical density greater than 2 at both of these bands. When cooled to liquid nitrogen temperatures, an additional absorption band appeared at 12,500 Å. This however was considerably less dense than the F- and F'-band. KCl crystals examined demonstrated F- and F'-bands at 5400 Å and 8250 Å respectively both at room and liquid nitrogen temperatures. The KCl samples did not indicate the growth of additional bands when cooled to liquid nitrogen temperature as did the KI. In all samples, the bands covered on the order of 1000 Å; i.e., they were not sharply defined absorption peaks. Nine samples of KCl and three samples of KI were examined in this manner and results were consistent.

These same samples were then examined as intermodulation elements. The equipment with modifications was the same as utilized in the previous program. The optical setup was as shown in figure 17.

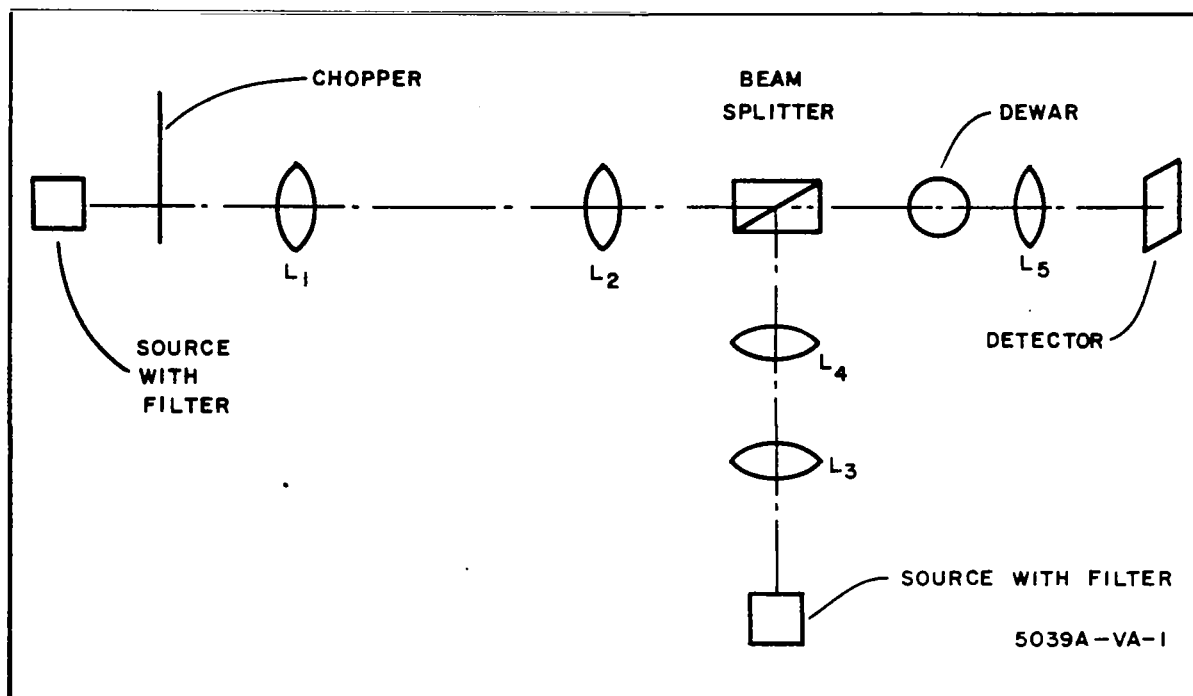


Figure 17. Experimental Arrangement for the Alkali-Halide Experiment

The electronics system was as shown in figure 18. Using an ac detection technique, it was possible to reduce the noise level of the detection system, as the system only responded to a signal of the same frequency of the chopping wheel. All other frequencies, including dc were rejected by the wave analyzer. This allowed the F^- and F'^- light to be incident on the same face of the crystal being examined without crosstalk. One source of difficulty, however, occurred if the F^- and/or F'^- light could saturate the detector or amplifier. This effect appeared as a reduction in the signal readout on the recorder and hence had to be guarded against, as it could be misinterpreted as intermodulation. In the initial phases of this investigation, this caused some difficulty, as this effect was interpreted as evidence of intermodulation. It was eliminated by ac coupling the silicon detector to the amplifier.

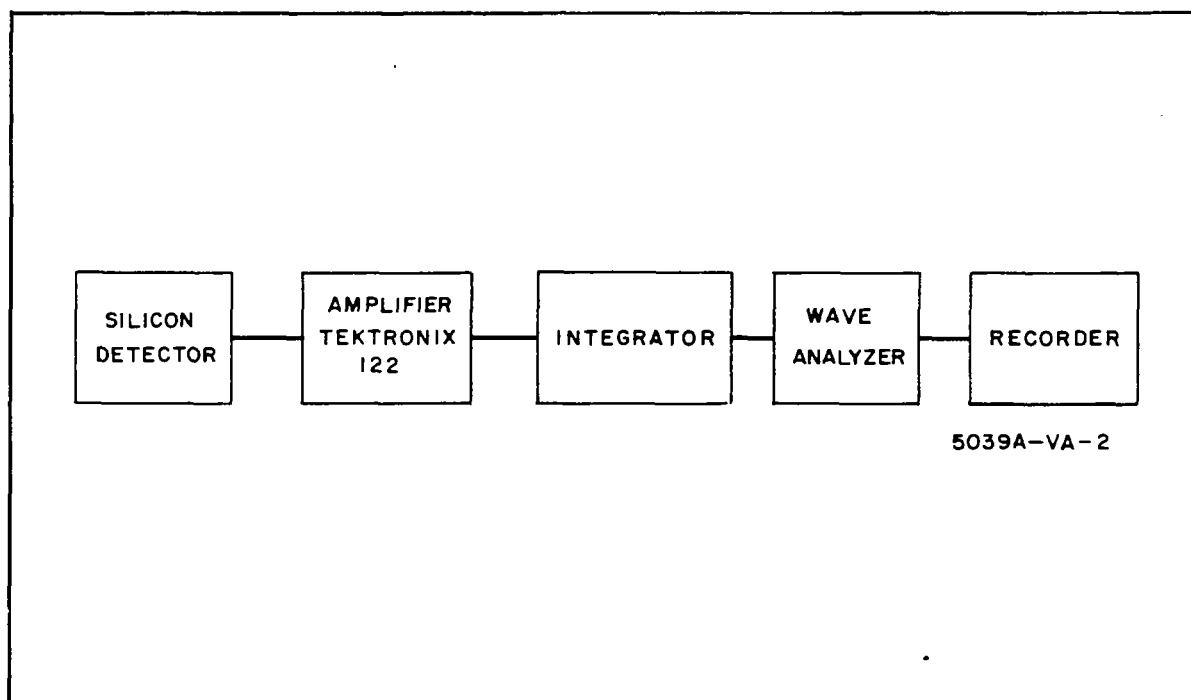


Figure 18. Block Diagram of Electronics

Using an EGG litemike, it was possible to obtain an estimate of the energy incident on the sample at 0.7μ . This was shown to be 11 microwatts with an energy density of $0.2 \text{ microwatt/cm}^2$ with 1 ampere current flowing in the lamp. Knowing the detector characteristics, it was possible to estimate the energy density incident on the sample at any wavelength. These values were equivalent to those used in the previous phase of the investigation.

Using this system, samples of KI and KCl were examined for evidence of intermodulation between the F- and F'-bands. At these light levels, it was not possible to observe any effects of intermodulation. Although the absorption of the crystals examined was high in the region of the F- and F'-bands, there was no evidence to indicate that the electronics could not detect a signal with a more than adequate signal-to-noise level. These experiments were conducted after long periods of allowing the system to come to equilibrium with the F'- and F-band being irradiated. These experiments also were attempted

using photographic flashbulbs with no noticeable effect. Again, sufficient time was allowed for equilibrium to be established between F- and F'-bands. Sampling was done in both the F- and F'-bands.

Considerations were also given to utilizing other ways of coloring samples of KI and KCl. Diffusion, electron bombardment, irradiation with X-rays, and ultraviolet are alternative methods of achieving coloring of the samples. Diffusion of the metal into these samples produces the most stable color centers. Diffusion, however, is not straightforward since it requires, among other things, a fast quench to freeze in the F-centers. This results in cracking and damages to the crystal surface which is difficult to remove. Therefore, this method of coloration was not attempted.

Samples of KI were first irradiated with 120 kv X-rays for periods of exposure up to 15 minutes, (the time period which was limited by the X-ray machine characteristics). These samples exhibited no appreciable coloration when examined with the Carey 14 spectrophotometer. Using another X-ray machine, it was attempted to color samples using 45 kv X-rays from a copper target.^{59, 60} These samples were wrapped in 0.5-mil aluminum foil to prevent exposure to light, as well as to hermetically seal to some extent. These samples were exposed to X-rays for periods of approximately 2 hours.

Samples of KI colored in this manner were examined with the Carey 14 spectrophotometer at room temperature. This examination indicated that appreciable coloring at 6943 Å had been achieved with an optical density of approximately 0.96. These samples had never been exposed to anything but a red safelight prior and subsequent to this examination. By setting the monochromator at 6943 Å and opening the slit to its full 3 millimeter width, it was possible to demonstrate the growth of the F'-band at 11,000 Å with the simultaneous reduction of the F-band. This growth of the F'-band and reduction of the F-band was a slow process proceeding exponentially with time. Subsequent irradiation with the monochromator at 11,000 Å for equivalent periods of time results in the disappearance of the F'-band but no regrowth of

the F-band. Typical times of irradiation at these wavelengths were 35 to 45 minutes.

This sample was then examined in the setup shown in figure 17. These experiments were conducted at both room and liquid nitrogen temperatures. In all cases, no intermodulation of any significance was observed.

Additional samples were then irradiated as described above with 45 kv X-rays and examined as intermodulation elements. These were also examined at room and liquid nitrogen temperatures. Again no evidence of significant intermodulation was indicated.

These samples were then examined with the Carey 14 spectrophotometer. The F-band at 6943 Å was present but there was no evidence of the F'-band. Furthermore, exposure to 6943 Å radiation did not produce a measurable F'-band at 11,000 Å. In addition, the height of the absorption band had decreased by more than half.

Samples were also examined after being exposed to room light for varying periods of time and found still to have the F-band present, but not the F'-band. Furthermore, there was evidence of some bleaching of the F-band under irradiation at 6943 Å, but the extent of it was small and with a long time constant at room temperature. The F'-band did not appear.

Additional samples of KI irradiated with electrons from a Van De Graaff generator were examined using the Carey 14 spectrophotometer. These samples exhibited a band at 6943 Å and one at 11,000 Å as did the others; however, it was not possible to demonstrate the increase and decrease of these bands as the samples were irradiated. Exposure to room light did not alter the F- and F'-band measurably, but exposure to an intense movie-projector-type bulb at close range did have the effect of diminishing the absorption in the region of 11,000 Å. This did not cause other bands to appear or alter the 6943 Å absorption band, indicating only that the F'-band at 11,000 Å is destroyed by this process.

6.3 SUMMARY

The experimental evidence of the last paragraph indicates that no fast, reversible intermodulation of KI or KCl was producible. The KCl crystals used in the experiment were heavily irradiated and it is likely that other centers predominated. The KI crystals, on the other hand, were colored under what appeared to be favorable conditions and any effect, if present, should have been absorbed; however, although in the case of KI irradiation in the F-band at 6943 Å caused a subsequent growth in the F'-band at 11,000 Å, indications were that, unlike earlier literature on the subject, the process appeared to require a long time. Furthermore, in the present series of experiments, it was never possible to observe a regrowth of the F-band by irradiation in the F'-band although the F'-band was bleached. Also, this bleaching required an equivalently long time using the Carey spectrophotometer as a monochromator.

It is noteworthy that any bleaching effects were observed only in the KI samples which were irradiated with 45 kv X-rays from a copper target.⁶⁰ Samples colored by electron bombardment, while showing F- and F'-absorption bands, must have contained other impurity centers which masked the effect of F- and F'-absorption. Reinberg and Grossweiner⁶⁰ noted a decrease in the bleaching ability of KCl crystals after exposure to the bleaching light at room temperature and attributed this to the presence of M-centers. Possibly, high energy bombardment created more impurity centers than were desired. The crystals colored by 45 kv X-rays, on the other hand, showed two clear absorptions; one of which could be bleached. It is otherwise difficult to state why the results of the experiment were not in agreement with Grossweiner^{59, 60} who concluded that "the relative concentration of color centers can be temporarily displaced in either direction by a light pulse of appropriate wavelengths."

7. CONCLUSIONS

At the end of the MIROS programs, the following conclusions can be drawn.

- Passive optical modulation is possible. This has been demonstrated both theoretically and experimentally.
- It is possible, by a suitable choice of materials, to cover almost any desired spectral region. This 3-month study program indicates only a small portion of the many organic compounds which are potentially able to transfer optical modulation passively. Many of these materials are beginning to find practical applications in laser Q-switching, data storage units, light projectors, etc.
- The power required to produce appreciable modulation need only be milliwatts. The mercury cell was able to effect 50-percent modulation with incident driving power of the order of a milliwatt. Organic materials may achieve similar results. Bloom's modulation scheme using doublet lines may be noted here. He speculated that energy, corresponding to hyperfine transitions could be used to modulate an optical transition.
- Modulation rates are moderately high. The upper limits would probably be in the megacycle region. The mercury absorption cell (MIROS Technical Data Report), the only system of its type (i.e., singlet-triplet scheme) tried experimentally, was able to follow easily kilocycle sine waves without noticeable distortion and response times of some organics are also promising. Of course, modulation rates depend on state lifetimes, transition probabilities, and optical intensities.
- One of the most efficient schemes makes use of a 4-level system: ground, first excited, metastable, and second excited states. This offers the advantage of choosing a large ground state absorption coefficient (provided a high transition probability between first excited and metastable states can be produced); hence, high quantum efficiency.
- The alkali halide schemes, while theoretically attractive for many reasons, do not appear to be as satisfactory as some other schemes.

A study of coloring techniques might improve their performance, as might clever additions of impurities. However, there are so many other promising materials that it would be difficult to justify giving priority to another alkali halide developmental program.

- Other schemes, such as passive induced modulation by means of creating free-charge carrier populations have been demonstrated, although not during the MIROS program. These are most effective when the modulated beam lies in the infrared. Here again, however, a materials development program might produce a greater variety of possibilities.

8. RECOMMENDATIONS

During the course of this investigation, materials have been found (organic compounds) which show every indication of providing a passive optical modulation transfer system. The power considerations appear moderate (milliwatt region) and modulation rates in the megacycle region should be attainable. Within these modulation rate and incident power level constraints, communications systems for various applications should be realizable.

In addition, this basic passive optical modulation may very well have application to other areas and optical devices. Possible uses are as radar duplexers, radiation detectors in otherwise inaccessible spectral regions, information storage devices, computers, optical logic circuits, high speed photography, etc.

It is recommended that additional effort be applied toward the development of breadboard models of these passive modulators for specific communications systems or other devices as indicated above.

9. BIBLIOGRAPHY

1. "Infrared Spectra of Phthalocyanines With Different Central Metal Atoms," Spectrachimica Acta Suppl, 1957, pp 573-578.
2. "Phthalocyanine Crystal Spectre," J. Chem. Soc., 1960, pp 167-175
3. G.P. Gurinovich, A.N. Sevchenko, and Solov'ev, Soviet Physics Uspekhi, Vol. 6, No. 1, 1963, p. 67.
4. U.L. Ermolaev, "Energy Transfer in Organic Systems. Involving the Triplet State, III, Rigid Solutions and Crystals," Soviet Physics Uspekhi, 1963-1964, pp 333 and 357.
5. M.L. Pool, "Life of Metastable Mercury and Evidence for a Long-Lived Metastable Vibrating Nitrogen Molecule," Physical Review, Vol. 38, September 1931.
6. A. Stern and H. Molrig, Z. Phys. Chem., A176, 209, 1936, p. 209.
7. J.B. Allison and R.S. Becker, J. Chem. Phys., Vol. 32, 1960, p. 1410.
8. R.S. Becker and M. Kasha, J. Am. Chem. Soc., Vol. 77, 1955, p. 3669.
9. R.G.W. Norrish and G. Porter, Nature, Vol. 164, 1948, p. 658.
10. G. Porter, Proc. Royal Soc. (London), A200, 1950, p. 284.
11. R. Livingston and V.A. Ryan, J. Am. Chem. Soc., Vol. 75, 1953, p. 2176.
12. E.W. Abrahamson and H. Linschitz, J. Chem. Phys., Vol. 23, 1955, p. 2198.
13. R. Livingston, J. Am. Chem. Soc., Vol. 77, 1955, p. 2179.
14. R. Livingston, G. Porter, and M. Windsor, Nature, 173, 1954, p. 485.
15. L. Pekkariinen and H. Linschitz, J. Am. Chem. Soc., Vol. 82, 1960, p. 2407.
16. L.S. Forster and R. Livingston, J. Chem. Phys., Vol. 20, 1952, p. 1315.
17. L.S. Brody and E. Rabinowitch, Science, Vol. 125, 1957, p. 555.
18. R. Zito and A.E. Schroeder, "Optical Excitation of Mercury Vapor for the Production of Isolated Fluorescence," Applied Optics, Vol. 2, No. 12, December 1963.

19. E.W. Samson, "Effects of Temperature and Nitrogen Pressure on the Afterglow of Mercury Resonance Radiation," Physical Review, Vol. 40, June 1932.
20. R. Livingston, Watson, and McArdle, J. Am. Chem. Soc., Vol. 71, 1949, p. 1542.
21. J. Fernandez and R.S. Becker, J. Chem. Phys., Vol. 31, 1939, p. 467.
22. J.B. Allison and R.S. Becker, "Effects of Metal Atom Perturbations on the Luminescent Spectra of Porphyrins," J. Chem. Phys., Vol. 32, No. 5, May 1960, pp 1410-1417.
23. H. Linschitz and K. Sarkanen, "The Absorption Spectra and Decay Kinetics of Metastable States of Chlorophyll A and B," J. Am. Chem. Soc., Vol. 80, 1958, p. 4826.
24. R. Livingston and E. Fujimori, "Some Properties of the Ground Triplet State of Chlorophyll and Related Compounds," J. Am. Chem. Soc., Vol. 80, November 1958, pp 5610-5613.
25. R. Livingston, "Preliminary Study of a Metastable Form of Chlorophyll in Fluid Solutions," J. Am. Chem. Soc., Vol. 77, 1955, pp 2179-2182.
26. L. Pekkarinen and H. Linschitz, "Studies on Metastable States of Porphyrins, II. Spectra and Decay Kinetics of Tetraphenylporphine, Zinc Tetraphenylporphine, and Bacteriochlorophyll," J. Am. Chem. Soc., Vol. 82, 1960, pp 2407-2411.
27. "Long Time Phosphorescence of Organic Crystal," J. Chem. Phys., June 1955, pp 1043-1047.
28. G.R. Seely and M. Corbine, "Photochemical Studies of Porphyrins, III. Photoconduction of a Porphyrin by Benzoin," J. Chem. Phys., Vol. 23, 1955, p. 1068.
29. R. Livingston, "Infrared Spectra of Chlorophyll and Related Compounds," J. Am. Chem. Soc., Vol. 75, 1955, p. 2173.
30. "Line Spectra of Polycyclic Aromatic Hydrocarbons in Frozen Crystalline Solutions," Optics and Spectroscopy, Vol. XIII, No. 3, September 1962, pp 188-193.
31. "On the Antistokes Phosphorescence of Organo-Phosphors," Optics and Spectroscopy, Vol. IX, No. 2, December 1960, pp 396-397.
32. "The Luminescence of Simple Derivations of Benzene I, The Aromatic Amines," Optics and Spectroscopy, Vol. XI, No. 4, 1961, pp 266-269.
33. "The Light Absorption and Fluorescence of Triarylmethyl Free Radicals," J. Am. Chem. Soc., Vol. 66, 1944, p. 1985.

34. "Studies on Fluorescence and Photosensitization in Organic Solutions III," Proc. Royal Soc. (London), A121, 1928, p. 313.
35. J. Am. Chem. Soc., Vol. 66, 1944, p. 1579.
36. Phy. Rev., Vol. 27, 1926, p. 804.
37. Phy. Rev., Vol. 28, 1926, p. 684.
38. Proc. Royal Soc. (London), A121, 1928, p. 294.
39. Phy. Rev. Letters, Vol. 8, 1962, p. 8.
40. G. Lewis and M. Kosha, "Phosphorescence and the Triplet State," J. Am. Chem. Soc., Vol. 66, December 1944, pp 2100-2116.
41. "Absorption and Re-emission of Light by CIS and Transstilbenes and Efficiency of Their Photochemical Isomerization," J. Am. Chem. Soc., Vol. 62, November 1940, pp 2973-2980.
42. G. Lewis, "Reversible Photochemical Processes in Rigid Media; A Study of the Phosphorescent State," J. Am. Chem. Soc., Vol. 63, November 1941, pp 3005-3018.
43. G. Lewis and M. Kosha, "Phosphorescence in Fluid Media and the Reverse Process of Singlet-Triplet Absorption," J. Am. Chem. Soc., Vol. 65, 1943, p. 1150.
44. P. P. Sorakin, et al, "Ruby Laser Q-Switching Elements Using Phthalocyanine Molecules in Solution," IBM J. Res. Dev., Vol. 8, April 1964, p. 182.
45. D. Kofalis, et al, "Photosensitive Liquid Used as a Nondestructive Passive Q-Switch in a Ruby Laser," J. Appl. Phys., Vol. 35, August 1964, p. 2349.
46. "Giant Pulse Laser and Light Amplifier Using Variable Transmission Coefficient Glasses as Light Switches," Appl. Phys. Letters, Vol. 4, 15 May 1964, p. 175.
47. Bull. of Am. Phys. Soc., Vol. 9, 1964, p. 66.
48. Jablonski, Z. Physik, Vol. 94, 1935, p. 94.
49. Lewschin and Vinokurov, J. Am. Chem. Phys., Vol. 10, 1936, p. 10.
50. A. V. Karyahin and A. N. Terenin, "Problems of Photosynthesis," Reports of the Second All-Union Conference on Photosynthesis, Moscow 1957, (AEC-TR-4501 in AEC Translation Series).
51. Garrola, Z. Physik, Vol. 42, 1927, p. 835.
52. Weber, Z. Physik, Chem., B15, 1931, p. 15.
53. Weber, Z. Physik, Chem., B30, 1935, p. 69.

54. Frauch and Lerr, Z. Physik, Chem., B27, 1935, p. 409.
55. L.A. Hall and G.H. Dicke, "Fluorescent Lifetime of Uranyl Salts at Different Temperatures," J.S.A., Vol. 47, No. 12, December 1957.
56. E. Goviola, "The Power Relation of the Intensities of the Lines of the Optical Excitation of Mercury," Philosophical Magazine, Vol. 6, 1926, pp 1154-1167.
57. R.B. McQuistan and J.W. Schulz, "Modulation of Infrared by Free Carrier Absorption," J. Appl. Phys., Vol. 35, No. 4, April 1964, p. 1243.
58. R. Lawrence and A.F. Gibson, Proc. Phys. Soc., B65, 1952, p. 65.
59. A. Costikas and L.I. Grossweiner, "Photoequilibrium Between KCl F and F' Centers at 80°K," Phys. Rev., Vol. 126, No. 4, May 1962, p. 1410.
60. A.R. Reinberg and L.I. Grossweiner, "Low Temperature Bleaching of F Centers in KCl," Phys. Rev., Vol. 122, No. 6, June 1961, p. 1734.
61. F. Seitz, "Color Centers in Alkali Halide Crystals, I," Review of Modern Physics, Vol. 18, No. 3, July 1946.
62. F. Seitz, "Color Centers in Alkali Halide Crystals, II," Review of Modern Physics, Vol. 26, January 1954.
63. G.H. Dicke and A.B.F. Duncan, Spectroscopic Properties of Uranium Compounds, McGraw-Hill Book Co., Inc., 1949.
64. G.K. Rollefson and M. Burton, Photochemistry and the Mechanism of Chemical Reactions, Prentice-Hall, Inc., 1946.
65. E. Robinowitch and R.L. Belford, Spectroscopy and Photochemistry of Uranyl Compounds, The MacMillan Company, 1964.
66. A.C.G. Mitchell and M.W. Zemansky, Resonance Radiation and Excited Atoms, Cambridge University Press, 1961.
67. T.S. Moss, Optical Properties of Semiconductors, Butterworth and Company, Ltd., 1961.
68. P. Pringsheim, Fluorescence and Phosphorescence, Interscience Publishers, Inc., 1949.
69. N.F. Mott and R.W. Gurney, Electronic Processes in Ionic Crystals, Dover Publications, Inc., 1964.
70. Research on a Passive Modulation Inducing Retrodirective Optical System (MIROS), Final Report, Westinghouse Electric Corporation, (Contract NASw 703), 1964.